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Environment
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Jim Bradley, Minister

PROCEEDINGS

SESSION C
LIQUID AND SOLID WASTE

November 28 & 29
Royal York Hotel
Toronto, Ontario
Canada

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SESSION C
LIQUID AND SOLID WASTE

Sponsored by
Research and Technology Branch
Environment Ontario
Ontario, Canada

Introduction

Environment Ontario holds its annual Technology Transfer Conference to report and publicize the progress made on Ministry-funded projects. These studies are carried out in Ontario Universities and by private research organizations and companies.

The papers presented at Technology Transfer Conference 1988 are published in five volumes of conference Proceedings corresponding to the following sessions:

SESSION A: AIR QUALITY RESEARCH
SESSION B: WATER QUALITY RESEARCH
SESSION C: LIQUID AND SOLID WASTE RESEARCH
SESSION D: ANALYTICAL METHODS
SESSION E: ENVIRONMENTAL ECONOMICS

This volume is comprised of presentations given during Session C of the conference.

For reference purposes, indices for sessions A,B,D and E may be found at the back of this volume, listed in alpha-numeric order.

For further information on any of the papers, please contact either the authors or the Research and Technology Branch at (416) 323-4574 or 323-4573.

Acknowledgements

The Conference Committee would like to thank the authors for their valuable contributions to environmental research in Ontario.

Disclaimer

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KEYNOTE PAPER I

Science-Based Innovation

Science-based innovation is critical in today's global economy to sustain and enhance a nation's prosperity. In seeking to sustain and enhance its prosperity by participating in a growing volume of world trade, large and small economies, face critical problems of adapting their institutions, policies and practices to a radically new environment. Key elements of this environment are that world trade now occurs in a global economy in which the interweaving of science, engineering and technology has acquired the power to transform the comparative advantage and prosperity of nations. With the scale, scope and openness of the international enterprise of science, the transferability of technologies and the mobility of capital, science-based innovation has become a driving force for the technological and corporate change that creates new tradeable goods and services. These conditions are radically different from those of the Industrial Revolution.

In a modern economy the sector which produces tradeable goods and services supported by the first service sector of financial, legal, energy, transportation, communication systems, etc., generates the income that enables a country to invest in the second service sector of education, health care and other personal and social benefits. (Figure 1). In some countries financial institutions have been operating in a manner that hampers the developments in the tradeable goods and services sector.

To participate in the global economy driven by science-based innovation it is essential that, on a national or regional basis, the pyramid of research capacity (in terms of knowledge flow) that leads to tradeable products and services has integrity, that is, that there be a reasonable balance of capacity throughout the pyramid. (Figure 2).

Increasingly science-based innovation requires a strong long-term applied research capacity, particularly in relation to emerging generic technologies, that is industry-based and controlled. This capacity has to be linked to a high quality fundamental research base and a strong market focused development capability.

Large and small countries in different stages of development faces problems in;

i) achieving structural integrity necessary for science-based innovation suitable for their limited resources of people and money, and

ii) using their limited resources effectively.

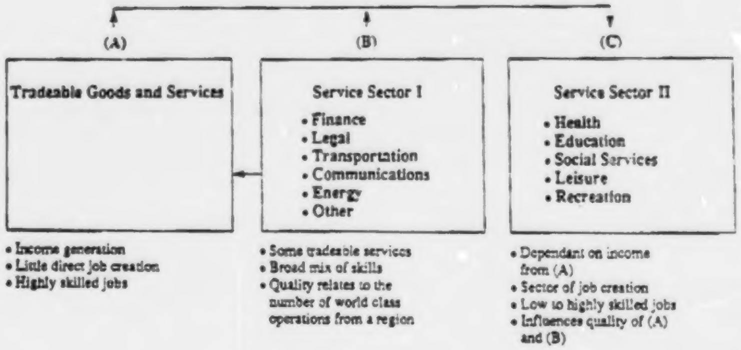
(A)
(B)
(C)
Tradeable Goods and Services
Service Sector I
• Finance
• Legal
• Transportation
• Communications
• Energy
• Other
Service Sector II
• Health
• Education
• Social Services
• Leisure
• Recreation
• Income generation
• Little direct job creation
• Highly skilled jobs
• Some tradeable services
• Broad mix of skills
• Quality relates to the number of world class operations from a region
• Dependant on income from (A)
• Sector of job creation
• Low to highly skilled jobs
• Influences quality of (A) and (B)

Figure 1: A Simple Model of the Economy

In today's global economy it is important to understand the relationship between innovation in the production of tradeable goods and services and the generation of income. A simple model in terms of stating the key issues is given in Figure 1. This model segments the economy into three blocks labeled (A) Tradeable Goods and Services, (B) Service Sector I and (C) Service Sector II. The major source of income which sustains our standard of living comes from sector (A) Tradeable Goods and Services. Canada's current standard of living requires very substantial volumes of trade into world markets. In the globally competitive market of today a nation must be concerned with maintaining and enhancing the environment it creates for business and industry that can innovate in the production of tradeable goods and services. To function effectively, such enterprises require a high quality service sector, namely (B) Service Sector I, comprising such services as finance, legal, energy, construction, communications, transportation, distribution. It is the combination of this business service sector (which produces some tradeable services) and the sector directly producing tradeable goods and services which generate the primary income of a region.

It is the income generated by the foregoing activities which allows the expansion of (C) Service Sector II that is concerned with personal and social services. The social service sector includes health care, education, community services, leisure and recreational activities. Our capacity to sustain and improve the services and opportunities depends on the capacity of sectors (A) and (B) to generate the necessary income.

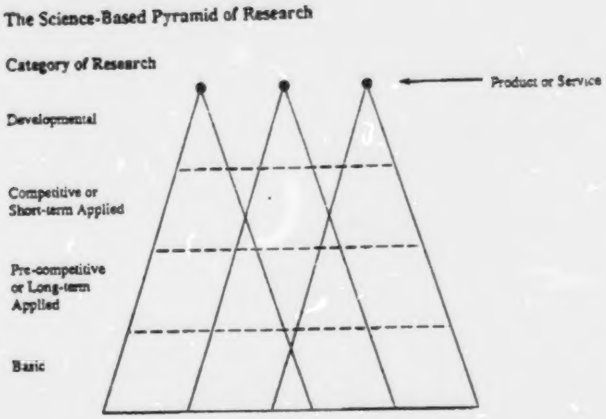
The Science-Based Pyramid of Research
Category of Research
Product or Service
Developmental
Competitive or Short-term Applied
Pre-competitive or Long-term Applied
Basic

Figure 2

Research as an element related to the overall process of innovation, can be broken down into three primary components that must be linked together to be effective:

1. Basic or fundamental research which is usually characterized by the researchers' primary objective being the generation of new knowledge and understanding about man and the world around us. This research is long-term (usually on a time-scale of 10 years or more), and has a high level of uncertainty in terms of what the results will be. In Western culture, basic research is primarily university-based and seldom results in knowledge that is of immediate commercial value. The knowledge gained from such research is rapidly and widely distributed to scientists throughout the world through publication in scientific journals. Because the results from this research are, or have been, considered a public good, this type of research has been financed primarily by the public sector and private benefactors. Increasingly, however, when knowledge contributed by basic research is critical for new product development, industries are becoming involved in basic research (OECD, 1987).

2. Applied research: In most countries, applied research is mainly carried out in industrial or government laboratories, but in some countries, there is substantial university involvement with respect to longer term research, particularly in schools of engineering, medicine and management. Applied research has a strategic target and attempts:

- to extend the scope of understanding of materials and processes,
- to determine how the accumulated knowledge from basic research, extend where necessary by focused specialized research, can be used to develop a potential new product or services, or
- to determine how to modify and improve the performance of existing products or services to sustain their marketability.

Applied research which is medium to long-term (on a time scale of three to ten years), also has a significant level of uncertainty, but because it is targeted, there is a probability that there will be economic benefit. The means for the financing of this research vary. In some sectors such as the pharmaceutical and chemical fields, the research is largely funded by the private sector primarily through the benefits from patent protection, whereas in fields such as aircraft and electronics, there has been a mixture of public and private financing. In some cases a monopoly position (e.g. AT&T and Bell Laboratories) has encouraged the funding of longer-term applied research, but there are few examples of the private sector being able to finance longer term applied research wholly from its own resources unless there is effective patent protection or the business has a monopoly position.

It is common in some sectors to associate the processes of engineering design and development of a product or service as discussed above, with the term development or developmental research.

3. Developmental research is research that:

- makes use of the fruits of applied research specifically to create a new markatable product or service, or
- improves, through a series of small steps of innovation based on state-of-the-art knowledge, an already existing product or service, or
- enhances the ease of production of a product or the provision of a service.

This type of research has the least uncertainty, is carried out on a time scale of less than three years, and has the highest probability of economic benefit. Developmental research is mainly financed by the private sector, although there are exceptions in which there has been substantial public financing.

The foregoing categories of research can be represented by the pyramids shown in Figure 2. At the narrow peak of each pyramid is a product or service, a specific artifact of technology designed to perform a particular function in a market. From its peak each pyramid expands through the three primary categories of research to a broad base in basic research. The category "applied research" has been segmented into two slices labeled competitive (short-term applied) and pre-competitive (long-term applied). Competitive applied research is that which has direct proprietary value to the business. Pre-competitive applied research is that which is generally useful in sectors of industry (This research is often concerned with what can be called generic technology). The relative width of each slice across the pyramid suggests the range of generality of the knowledge associated with it. The overlapping of parts of the pyramids indicates that as one reaches towards the scientific roots pertinent to the development of a particular product, the knowledge base becomes relevant to a range of products. Indeed, the essence of basic science is that it seeks for general principles of understanding within particular circumstances of study, whereas engineering, through the technology it creates, seeks to realize a particular operational function in a market within the domain of possibilities bounded by science.

Science-based innovation then is innovation in which the realization of an effective and competitive product or service utilizes, through the focusing processes of the pyramid of research, the full range of scientific and engineering understanding pertinent to the function of the product or service in the marketplace.

The classification of levels of research in the research pyramid of Figure 2 is based on the diverse literature on innovation. Its pertinence for older, large-scale, science-based industries is clear. However, a key point today is that the research pyramid is relevant to all industry participating in the global economy of science-based innovation.

Copies of "INNOVATION AND CANADA'S PROSPERITY: THE TRANSFORMING POWER OF SCIENCE, ENGINEERING AND TECHNOLOGY" may be obtained by filling out the attached form.

KEYNOTE PAPER II

DERIVING BENEFITS FROM ENVIRONMENTAL RESEARCH

Stuart L. Smith, M.D.
President
RockCliffe Research and Technology Inc.
November 1988

As difficult as research can be, it is still more difficult to apply it swiftly for economic or social benefit. In addition to the usual obstacles to technology transfer, environmental research faces additional ones of a political nature. It behooves us to know a great deal more about how research is transformed into practical benefits and how environmental research in particular can be more rapidly applied. The improvement of the environment is an area where, with appropriate policies, economic and social benefits occur simultaneously.

In supporting research activities, we cannot take for granted that application will naturally follow any improvement in knowledge. More attention needs to be paid to the incentive structures of research organizations, the relationship to our industrial sector, and the interaction with political decision-making. By acting now in some specific areas, we can help guarantee that today's research will produce timely and tangible results.

SESSION C

LIQUID AND SOLID WASTE RESEARCH

Oral Presentations

ENVIRONMENT ONTARIO PAPER

LIQUID AND SOLID WASTE RESEARCH

Ulo Sibul
Waste Management Branch
Environment Ontario

Research needs in the handling, treatment and disposal of liquid and solid wastes not conveyed to municipal sewage treatment plants are necessarily as diverse as the materials that make up the waste streams.

Future research needs identified by the Ministry of the Environment fall into one or more of three broad categories:

Waste Handling
Waste Reduction
Landfill Technology

A total of fifteen general issues have been identified within these categories.

It is important that waste materials have all pertinent characteristics determined so that the need for treatment, the appropriate method of treatment and the required degree of treatment can be accurately identified.

Having identified a need for some type and degree of treatment, it has become necessary to develop and demonstrate the appropriate treatment methodologies.

The best case situation occurs when there is no waste to treat. This is an unrealistic goal but there is a recognized need to investigate, develop and demonstrate the so-called "4 R's" of waste management, the reduction, recycling, recovery and re-use of waste materials.

Landfill sites will continue to be the ultimate repository of residual wastes, treated or untreated, and it is a requirement to investigate, improve and enhance landfill technology to ensure safe and aesthetically acceptable disposal of the wastes that inevitably will occur. This has been a fruitful field of study in the past but will continue to deserve attention as our understanding of waste materials and behaviour expands. The control of contaminant migration from landfill sites and the safe containment of potentially dangerous wastes, including bio-medical wastes and incinerator ash requires study as does site rehabilitation and remediation for existing sites.

The ever increasing volumes of wastes makes this a challenging and rewarding subject for research.

C1

AN OVERVIEW OF RECENT RESEARCH RESULTS IN CONTAMINANT HYDROGEOLOGY AND IMPLICATIONS

John A. Cherry

Waterloo Centre for Groundwater Research
University of Waterloo
Waterloo, Ontario N2L 3G1

INTRODUCTION

Groundwater contamination is a major problem in nearly all industrialized countries. The problem has been developing for many decades but its existence generally went unrecognized prior to the 1980's. Groundwater in nearly all geological deposits travels slowly, less than 1 m per day and commonly less than 0.1 m per day. Thus, contaminants that enter the groundwater zone at waste-disposal sites, industrial sites, gas stations, septic systems and a wide variety of other common contaminant sources, normally take many years or decades to travel from the source to locations where they do recognizable harm, such as water-supply wells, springs or seepage zones feeding lakes or rivers. It is rare that groundwater contamination is discovered before harm occurs, even though the zone of groundwater contamination has been expanding for a long time prior to such discovery.

Much of what is now known about groundwater contamination has been learned during the past 10 years. With this new knowledge, the nature of the groundwater contamination problem has become clearer. The purpose of this paper is to briefly describe several major findings of recent years with comments on some implications of these findings.

DISPERSION

Dispersion is the process causing mixing of solutes in the groundwater zone. In sand or gravel aquifers where groundwater flow is primarily horizontal, a zone of contamination such as a plume undergoes mixing with uncontaminated water at its fronts. This frontal mixing is referred to as longitudinal dispersion. Mixing also occurs along the top and bottom of the plume, referred to as transverse vertical dispersion, and along the sides, referred to as transverse lateral dispersion. Field experiments conducted in a sand aquifer at Canadian Forces Base Borden, Ontario, indicate that, in this aquifer, dispersion in the two transverse directions is a very weak process resulting in almost no spreading of plumes laterally or vertically in the aquifer. Similar results have been obtained from other detailed dispersion studies in sandy aquifers elsewhere in Ontario, and on Cape Cod, Massachusetts. All of these studies and less detailed but nevertheless informative dispersion studies of sandy aquifers elsewhere have provided results consistent with the conclusion that dispersion in the transverse directions in sand and gravel aquifers is very weak.

An implication of this conclusion on transverse dispersion is that plumes of contamination emanating from point sources of contamination such as landfills, lagoons, chemical spills, leaky gasoline tanks and septic systems will commonly extend in the direction of groundwater flow as narrow discrete entities that follow the groundwater flow paths with little lateral or vertical spreading and with concentrations of some contaminants in the core of the plume that are not much diminished by mixing. In other words, for many types of point sources contributing persistent and hazardous contaminants to the groundwater zone, dilution in the groundwater zone is generally not an effective means of rendering the contamination innocuous even at distances of many kilometres from the source. Another implication of the results of dispersion research is that effective monitoring to detect off-site migration of contaminants is generally more difficult than previously thought because, for early detection, narrow plumes require monitoring wells to be situated at critical locations that cannot be reliably predicted when the monitoring system is installed in the aquifer.

MOLECULAR DIFFUSION

Prior to several years ago, it was commonly thought that contaminants could be contained at waste disposal sites by lining the site with a layer of compacted clay and by covering the top of the waste-filled site with a layer of compacted clay. Compacted, water-saturated clay commonly has a hydraulic conductivity approaching 10^{-8} cm/s. Under a hydraulic gradient of 1, such clay has an average linear groundwater velocity of about 1 cm/yr. This suggests that it would take 100 years for relatively mobile contaminants to pass through a 1 metre thick compacted clay liner. When the effect of molecular diffusion is taken into account, however, the time for a mobile contaminant to pass through the liner is only about 5 years for a 1 m thick liner and about 7 days for a liner that has a thickness of 0.1 m.

Foster (1975) was the first to recognize the importance of the influence of molecular diffusion on contaminant migration in groundwater in low-permeability deposits. Subsequent to Foster's research in Britain, researchers have determined the effects of molecular diffusion on rates of contaminant migration in Ontario clays (Goodall and Quigley, 1977; Desaulniers et al. 1981; Crooks and Quigley, 1984; Johnson et al. 1988). For water-saturated clay to provide long-term containment of many types of contaminants, the clay layer must have a thickness of many metres or more and must be devoid of open fractures. Designers of waste-disposal facilities in North America have generally been slow to recognize the influence of molecular diffusion on contaminant migration in designs for waste-isolation facilities which liners and caps are used to minimize escape of contaminants.

MOBILITY AND PERSISTENCE OF ORGANIC CONTAMINANTS

Prior to a decade or so ago, groundwater samples suspected of contamination were rarely analyzed for trace-level organic compounds. This was the case for several reasons, primary among them being the fact that the sophisticated laboratory facilities necessary to do such analyses were rare in water-quality laboratories in nearly all industrialized countries. These facilities did not come into significant use in Canada until the mid-1980's and even now only exist in a few provinces.

From trace-organic analyses of groundwater done in many countries, it is now known that (1) that groundwater contamination is much more common in most industrialized countries, than was previously suspected and (2) that, when groundwater is found to be contaminated to a degree potentially harmful to the health of water users, it is usually due to trace organic compounds. Nearly all organic contamination of groundwater has originated since the Second World War. In the 1950's the use of petroleum products and halogenated organic liquids rapidly became commonplace in cities, towns and villages.

The organic contaminants most frequently found in groundwater are listed on Table 1. Of these, the volatile organics are the most common because they are relatively persistent and have little affinity for adsorption in aquifers. Many of these compounds are carcinogens and have drinking-water limits specified in Europe or the United States at the parts per billion or tens of parts per billion level. Leakage of very little mass of such compounds from waste storage or disposal facilities or from product storage containers at industrial sites can cause extensive contamination of aquifers at levels above such limits.

Analysis of groundwater in Canada for the compounds listed on Table 1 has lagged far behind many European countries and the United States because none of these compounds are included on the current federal drinking water standards issued in 1976, nor on provincial drinking-water standards, with the exception of Ontario where very recent changes have included some of them. As federal and provincial drinking water standards or guidelines in Canada are brought more in line with the recognition of the propensity for shallow groundwater to contain these organic compounds, we can expect analyses of well waters in Canada to include these compounds much more frequently.

The common aromatic hydrocarbons such as benzene, toluene and xylenes, derived from petroleum products often undergo fairly rapid biodegradation in aerobic groundwater zones. Biodegradation can cause the contamination to be restricted to a zone close to the contaminant source. Unfortunately, many contaminated aquifers are anaerobic, a condition that promotes the persistence and therefore extensive migration of these compounds.

The common chlorinated volatile organics such as tetrachloroethylene, trichloroethylene and trichloroethane generally do not biodegrade rapidly in aquifers. These compounds tend to slowly transform to less chlorinated but nevertheless hazardous compounds. In some cases the transformation products are more hazardous in drinking water than the original compounds.

DENSE IMMISCIBLE LIQUIDS

Many of the chlorinated compounds on Table 1 enter groundwater as immiscible liquids that are more dense than water. These oil-like liquids then dissolve and are transported by groundwater away from the source. Examples of dense immiscible liquids are chlorinated solvents, creosote, coal tar, and PCB liquids. Most common chlorinated solvents are less viscous than water and with their high density flow quickly downward through permeable soil into shallow aquifers, where they can settle below the water table on top of strata of low permeability. Small volumes of these immiscible liquids settled out in an immobile state in an aquifer can take a long time to disappear. For decades or even centuries the immiscible liquid will continue to dissolve in the aquifer and thereby feed contaminants to the flowing groundwater.

SOURCES OF CONTAMINATION

Of the many causes of groundwater contamination, only two will be discussed here, sanitary landfills and domestic septic systems. Leachate from sanitary landfills commonly contains a variety of mobile organic compounds, including many of those listed on Table 1. This seems to be the case even for landfills where disposal of hazardous industrial wastes are prohibited. The quantities of industrial organic liquids necessary to cause high concentrations in leachate are so small that prevention of their entry to municipal landfills is not feasible.

Leachate production in municipal landfills occurs for centuries. In wet climates such as in Ontario, the ability of landfills after closure to produce leachate containing hazardous levels of organic compounds listed on Table 1 is not known. I expect that the time scale is many decades or centuries. With such time scales, it is reasonable to expect that many, if not most, municipal landfills in Ontario will eventually cause offsite migration of some of the volatile organic compounds listed on Table 1. This statement is applicable even to municipal landfills of the most modern design if they are situated on geologic deposits than are not exceptionally impervious.

For a domestic on-site septic system to be approved in Ontario, the drainbed and subsoil must provide sufficient infiltration capacity for the subsurface to accept all of the effluent from the septic tank. In most hydrogeologic settings in Ontario, the effluent infiltrates to the water table and then moves primarily laterally in the groundwater regime.

Some contaminants, most notably sodium, chloride and nitrate, can travel large distances laterally, such as hundreds of metres, at relatively high concentrations. The drinking water limit for nitrate is 45 mg/L as NO_3^-. Research conducted recently by the University of Waterloo indicates that nitrate plumes from single-family homes situated on sand or gravel deposits or on fractured bedrock can be expected to cause off-property degradation of groundwater quality, with nitrate levels generally above the drinking water limit. The research has not yet progressed to the point where the type and persistence of aromatic and chlorinated organic contaminants in septic plumes can be predicted.

A septic system and a shallow water supply well serving the same household are common in Ontario and in most parts of North America even though the distance separating the two, which is mandated in regulations, is not adequate to prevent contamination of the well by the septic system. Commercial chemicals commonly sold in Ontario for cleaning of plumbing connected to the septic system contain hazardous organic compounds even though such compounds may cause severe groundwater contamination. In some states in the U.S.A., the sale of septic-system plumbing cleaners containing hazardous organic chemicals is banned.

CONCLUSIONS

In the past decade groundwater research and monitoring of groundwater supplies in industrialized countries has shown that groundwater contamination is a greater problem than was previously thought. The most common groundwater contaminants capable of causing significant adverse health effects on persons who drink the water are nitrate and volatile organics. These and some other contaminants in groundwater are commonly mobile and little attenuated in the groundwater because dilution (dispersion) and adsorption have only minor influences and biodegradation is commonly ineffective. The problem is exacerbated by the fact that dense immiscible liquids are ubiquitous in industry. Many of these liquids rapidly enter aquifers if spilled or leaked on the ground in even small quantities. Groundwater contamination is caused by chemicals entering the groundwater zone from many types of sources. Some causes are accidental; others are the normal product of the generally-accepted design of the system, such as municipal landfills and on-site septic systems. Monitoring of volatile organic compounds in groundwater is in an early stage in Canada. The true nature of groundwater contamination in Canada will become more evident as such monitoring becomes more widespread and frequent, as it already has in the United States and some European countries.

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Table 1: **List of trace organic compounds most frequently found in contaminated groundwater**

Volatile Organics
Benzene
Ethyl benzene
Toluene
Xylenes

Carbon tetrachloride
Chloroform
Dichloromethane

1,1,1-Trichloroethane
1,2 Dichloroethane
1,1-Dichloroethane
Chloroethane

Tetrachloroethylene
Trichloroethylene
Trans-1,2-dichloroethylene
1,1-Dichloroethylene

Chlorobenzene
Dichlorobenzenes (1,2-, 1,3- and 1,4- isomers)

Phenols
Total Phenols
Cresols (2-methyl, 3-methyl and 4-methyl isomers)
Pentachlorophenol
Phenol

Polynuclear Aromatic Hydrocarbons
Naphthalene

C2

IMMISCIBLE LIQUIDS AND VAPOURS IN SOIL: RECENT EXPERIMENTS ON TRANSPORT AND CONTROL

G. Farquhar, R. Benson, R. Kell,
E. McBean, B. Stickney and D. Farrish

Department of Civil Engineering
University of Waterloo
Waterloo, Ontario, N2L 3G1

ABSTRACT

This paper provides a summary of some recent results from an on-going research programme studying the transport and control of hazardous immiscible liquids and their vapours in soil environments. Results are presented on the transport of pentane vapours from two different liquid source configurations within a long, thin chamber containing dry sand. The results were then successfully simulated using a two-dimensional mathematical mass transport model and these simulations are shown graphically. The paper also provides preliminary results from laboratory scale experiments examining air venting as a means of removing volatile solvents from soil. One such experiment involves an air purge of 50 cm of sand with the lower quarter of the column containing hexane at residual saturation. The results show an increase in hexane content of the exhaust gas to near ambient vapour pressure and then a decrease as the liquid in the soil reaches depletion. A mass balance showed a nearly complete recovery of the hexane. Subsequent experiments have studied the impact of air flow rate, source geometry and air flow configuration on recovery efficiency. Experimental work has also been done to examine vapour adsorption on soil and recent results are presented.

INTRODUCTION

This paper presents some recent results of studies on the behavior of immiscible liquids and their vapours in soil. This is part of a research programme that has been underway for the past four and one-half years at the University of Waterloo in the Department of Civil Engineering. The work has been jointly supported by the Ontario Ministry of the Environment (Project No. 334PL) and the Natural Sciences and Engineering Research Council (NSERC).

While both liquid and vapour behavior are being examined as a part of the research programme, this paper deals primarily with recent vapour investigations. Three distinct topics are addressed.

1. Testing the suitability of a previously developed vapour transport model to simulate laboratory experimental results on hazardous vapour movement in soil.

2. The design and use of experiments to study the adsorption of vapours onto soil.

3. Experiments to investigate the parameters which affect the design and performance of forced air venting systems to remove volatile organic solvents from soil.

The equipment and experimental results for topic 1. have been described previously (Farquhar *et al.*, 1987). The model simulations and all of the information presented on topics 2. and 3. have however not been presented prior to this.

SIMULATION OF EXPERIMENTS ON VAPOUR TRANSPORT IN SOIL

Two types of experiments were completed in the study of vapour transport through soil; one involving a vertical column of soil, 7.0 cm in diameter and 36.0 cm long and the other using a rectangular flux chamber, 3.7 m long, 1.2 m high and 0.15 m wide. These pieces of equipment, shown in Figures 1 and 2 respectively, and their operation have been described in detail elsewhere (Farquhar, *et al.*, 1987) and only a brief summary is given here. It was possible with the column to add a vapour source to either the top (headspace) or the bottom (footspace) of the column and then to observe its movement through the soil sample by means of vapour extraction at the sampling ports. Pressure measurements across the soil column were also taken. Soils included dry sands (moisture content < 1% w/w) and methane as a gas and pentane, hexane and acetone as vapours from liquid sources were used. The duration of the experiments ranged up to 95 hours.

The same soils and vapours were also used in the rectangular flux chamber. It was possible to introduce vapours at the base of the chamber to simulate vapour movement away from a pool of solvent perhaps lying on the zone of saturation. The apparatus for generating a bottom vapour source consisted of a prismatically shaped tray in which variable liquid surface areas could be maintained. Vapours moved upward from the tray through a stainless steel screen and into the soil. A second device was used to simulate a liquid vapour source suspended above the zone of saturation. This involved an external flask containing liquid connected to a perforated teflon tube inside the chamber. Vapour produced in the flask moved through the pipe and into the chamber. Vapour transport throughout the chamber was detected with the use of syringes inserted at the sampling ports shown on Figure 2. Gas chromatography served to quantify vapour concentrations in the samples collected.

The data collection programme encompassed over 30 experiments in which vapour transport away from the source was measured. Transport model simulations were performed on several of these and samples of these simulations comprise a part of this paper.

1. The Vapour Transport Model

The vapour transport model (AD2D) used in these simulations is an adaptation of an earlier model developed as a part of this research programme (Allan *et al.*, 1985). The model solves equations for fluid flow through porous media in two dimensions based on the principles established by Bear (1972) with vapour concentrations expressed on a molar basis. Density driven flow resulting from body forces, diffusion as well as pressure gradient flow, variability in soil type and soil moisture content and reactions between soil and vapour are all features which have been incorporated into the model. Either concentration specified (Dirichlet) or flux specified (Cauchy) conditions can be specified at the soil boundaries. Solution to the partial differential equations is achieved through the use of finite element methods and, in particular, the Galerkin Method of Weighted Residuals.

The original model was adjusted by Kell (1988) for execution on a personal computer (IBM PC compatible) with 360 k memory. It was revised to accommodate transient pressure distributions to account for density dependent flow and was used in this form for all simulations.

2. Simulation of Experiment Results

The data on soil and vapour properties used in the simulations are summarized in Table 1. Finite element size and shape and time steps used are described elsewhere (Kell, 1988).

2.1 Column Experiment Simulation

The information in Figure 3 involves the downward transport of acetone vapours through a vertical column of sand from a liquid source in the headspace. The average acetone vapour concentration at the source (C_0) was 15.1% v/v. The upper portion of the figure shows actual data collected at the sampling ports after 25, 45, 100 and 200 minutes. The nonlinear shapes of the curves are consistent with transport induced by both diffusion and density driven flow. The density of acetone is greater than that of air and thus a downward force was operative. Diffusion only, as seen with the experiments on the downward transport of methane (lighter than air), produced linear relationships on similar plots (Farquhar, *et al*., 1987).

The lower portion of the curve shows AD2D model simulations of the actual data measured at 200 minutes. The simulation with only diffusion and body force induced transport with Dirichlet boundaries at both the top and bottom of the column did not fit the data well. The fit was improved with the inclusion of a source pressure (ΔP) = 5.0 Pa (pressure gradient of 13.3 Pa.m^{-1}). This is a very small pressure gradient and not detectable with the manometers in use at the time of experimentation. Although the source headspace was open to the atmosphere through 2-10 cm orifices, some pressure buildup due to acetone volatilization could be expected. More recent experiments using a pressure transducer did detect small pressure accumulations in the range from 5 to 10 Pa.

A sampling port located at the bottom of the column between the sand and the supporting screen yielded acetone vapour concentrations on the order of 1% v/v as opposed to the 0% v/v concentration Dirichlet boundary condition assumed in the simulation. Thus a Cauchy flux boundary appeared to exist at this outlet point of the column. Although the AD2D model can accept a Cauchy flux boundary at the outlet, there were no means available at the time to quantify this flux.

Experimental results and their simulation are shown in a similar way on Figure 4 for the upward transport of acetone from a bottom liquid source. Early in the experiment (at 25 and 45 minutes) the nonlinear nature of the transport is quite evident. Because acetone vapour is heavier than air, it is accumulating more in the lower portion of the soil and is moving upward by diffusion and possibly due to a small pressure gradient. As shown in the lower set of curves simulating the vapour position after 200 minutes, the addition of a $\Delta P = 5$ Pa improved the simulations greatly although this pressure head was below the detection limits of the equipment used.

In general, the ability of the model to simulate the one-dimensional column experimental data, given the inconsistencies in the input information noted above, was quite good. This also proved to be the case for other sand column experiments performed using methane and pentane as migrating vapours.

2.2 Two Dimensional Vapour Flux Chamber Experiments

Acetone as a Bottom Vapour Source

The information presented in Figure 5 shows experimental data and transport model simulations for acetone vapour movement in the two-dimensional flux chamber. The acetone source was a pool of liquid located beneath the soil at the midpoint of the chamber bottom. The sides and ends of the chamber were sealed while the top of the soil was open to allow vapour discharge. The data are presented as vapour concentrations in air as % v/v emanating upward from the 7% v/v vapour source. The concentration contours were found to be symmetrical about the centreline of the box and thus only one-half of the contours are shown from the source to one end of the chamber.

The upper figure presents the experimental data at 95 hours and demonstrates that the acetone vapours had moved upward and outward from the source toward the open top surface. Concentration contours range from 0.5 to 2.5% v/v and have shapes that are consistent with diffusional transport. The low slopes of the contours imply lateral movement due to body forces acting on a heavier vapour. No pressure build-up was detected at the source as the vapour moved outward into the air filled soil pores.

The lower figure shows the transport model simulations after 95 hours of experiment time. The simulated vapour concentration contours have the proper shape but tend to exceed the measured data at all concentrations. The simulations were carried out with Dirichlet boundary at the source and a Cauchy boundary using a radiation condition at the open surface. All input parameters were measured or estimated and no curve fitting was done. As a consequence, the transport model simulations were thought to be reasonably good.

Pentane as a Bottom Source

Experiments identical to those using liquid acetone as a bottom vapour source were performed with liquid pentane. Examples of the experimental results obtained are presented in Figures 6 and 7 for 24 and 72 hours of transport respectively. The upper portions of Figures 6 and 7 show the experimental data collected as concentration (% v/v) contours. The progress of the heavier pentane vapours moving through the previously air-filled soil pores is shown by comparing the two figures. From 24 to 72 hours, the contours have moved laterally and upward from the 18% v/v vapour source toward the open surface consistent with the diffusion of a heavier vapour. Lateral migration is shown to have occurred toward the sealed boundary at the left edge of the graph. Extensive lateral migration would be expected under certain field conditions.

The simulations performed at the two times are shown in the lower portion of the figures and are seen to be excellent. Once again, the simulations were performed with measured or estimated data and no curve fitting to the experimental data was performed. The transport model was judged to function extremely well in this case.

Pentane as a Suspended Source

The 2-D flux chamber was also used to simulate field situations where solvents have been spilled and remain as interstitial fluid within the vadose zone. This can then serve as a source for subsequent vapour transport. To accomplish this, a source of pentane vapour (11% v/v) was introduced at the centreline of the chamber and 0.75 m above the bottom. The movement of vapours away from the source was then tracked and is represented in Figures 8 and 9 for 12 and 72 hours respectively. The vapours are shown to have moved outward radially from the source with increased transport down and then outward. This is consistent with the diffusional together with the body force driven flow of a heavier-than-air vapour such as pentane. The progress of the vapours is seen through comparisons of the two figures. The vapours are being vented at the open top surface and excluded at the sealed left-hand boundary. The results confirm that such situations in the field could produce vapours at depths much greater than the actual spill location. These vapours could, in turn, then contaminate the groundwater through dissolution.

The transport model simulations performed for the two times are shown in the lower portions of the figures. These are seen to be excellent without the aid of curve fitting.

2.3 Comment

The experiments performed, a sample of which have been presented here, have demonstrated some important trends in vapour transport in soil. In particular, these relate to the relative impact of diffusional flow along concentration gradients, advective flow along pressure gradients and vertical flow due to body forces. The results are of value in spite of the specialized conditions of the work such as laboratory scale, single soil types, low soil moisture contents and single vapours.

The research has also shown that the 2-D vapour transport model, AD2D, is capable of producing excellent simulations of experimental results. The success of the simulations appear to be more dependent on the quality of the input information than on the model and its structure.

EXPERIMENTS TO ESTIMATE THE ADSORPTION OF VAPOURS ONTO SOIL

Part of this research effort was committed to developing methods and then using them to quantify the adsorption of vapours onto soil. The transport model AD2D has the capability of including vapour adsorption during transport but little data were available at the time of the study to allow inclusion of this process.

A method was developed based on the work of Thibodeaux (1984) and used for several adsorption experiments involving three soils, a clay, a well-graded sand and a poorly-graded Ottawa sand and several vapours including pentane, acetone and trichloroethylene (TCE).

The apparatus used and shown in Figure 10 consisted of a 21.4 L sealed glass dessicator fitted with a pressure release valve connected to a water seal. Samples of soil were added to 30 ml jars and the jars plus soil were then weighed and placed into the dessicator. Various volumes of liquid contaminant were placed in the bottom of the dessicator and the top of the dessicator was then sealed in place. The vapour concentration produced depended upon the volume of liquid added as did the pressure build-up in the dessicator. The vapour was allowed to be in contact with the soil for 24 hours and the residual vapour concentration was then determined through extraction at the sampling port. The dessicator was opened and the sample jars then sealed and weighed to determine increased weight due to vapour adsorption. Controls using soil-free jars were run to account for adsorption onto the glass. Tests were performed to quantify the time needed for equilibrium to be reached, the effect of mixing the soil and the extent of desorption under atmospheric conditions.

The results of the work were expressed as adsorption isotherms; mass of contaminant adsorbed (q) in g of contaminant per 100 g soil plotted against equilibrium vapour phase concentration (c) in % v/v. An example of the results obtained is found in Figure 11 showing Freundlich isotherms for acetone adsorbed onto sand (0.9% H_2O w/w) and clay (0.1% H_2O w/w). The saturated acetone vapour concentration in air was estimated to be approximately 26% v/v at the average experimental temperature of approximately 22° C.

The data in Figure 11 show that much more acetone was adsorbed onto the clay soil than onto the sand. The data follow the Feundlich form until a vapour concentration of approximately 18% V/V or about 70% of the vapour saturation in air. At this point, the apparent adsorption increased dramatically and this was found to be the case in all of the experiments run. The reason for this substantial increase is not known but it was speculated that vapour condensation was beginning to occur on the soil and that this, in turn, made it seem that the mass adsorbed was increasing.

Since the soils were extremely dry, the contaminant removal in the

Freundlich section of the curve was attributed to adsorption, the dissolution into pore water having been eliminated.

Similar results were obtained for other volatile chemicals and those for TCE are shown in Figure 12.

The results obtained from these experiments showed that adsorption of the chemicals used in the vapour transport experiments through sand was negligible. The adsorption component of the AD2D transport model was therefore not used in the simulations discussed in the previous section. Adsorption onto clay soils was however more significant and thus, the isotherms produced will be of use in simulations involving these soils.

Further studies will be performed with wet soils and the results compared to those of the current investigation. The separate quantification of dissolution and adsorption should be possible.

EXPERIMENTS ON THE USE OF FORCED AIR VENTING TO REMOVE VOLATILE ORGANICS FROM SOIL

Forced air venting is an important means for the removal of volatile organic liquids from soil either within the vadose zone or as a pool on top of the zone of saturation. There are frequent references in the literature to the use of forced air venting the field but little information is available on the fundamental processes involved;

1. The range of air flow rates possible.
2. The effect of spill shape and geometry on recovery efficiency.
3. The impact of soil type, stratification and moisture content on recovery efficiency.
4. The extent of contaminant recovery possible.

As a result, this laboratory scale research project was undertaken to examine some of these fundamental concerns and to assist the predictability of system performance. The work is still in progress but some preliminary results are available and these are presented subsequently. The work plan calls for the following experimental components:

1. One-dimensional columns and 2-D flux chamber experiments with equipment similar to that used in the vapour transport work.
2. Varying sizes and shapes of "spills".
3. Air flux rates ranging up to 4 L.cm^{-2}. hr^{-1}.
4. Soils ranging from coarse sand to sandy silt.
5. Soil moisture contents ranging from dry (1% H_2 w/w) to field capacity.
6. Two chemicals, hexane and TCE.

To this point in the research, several experiments have been performed using a 1-D column (60 cm long, 10 cm diameter), dry sand (K - 10^{-2} cm.s^{-1}) and hexane. Two rotometers one on the air intake and the other on the exhaust gas stream were used to measure gas flow rates while a pressure transducer detected pressure differences across the soil column. Two different methods were used to introduce hexane into the column.

1. Hexane Residual in Soil at the Column Base

Hexane was introduced into the bottom of the sand column to a height of approximately 14 cm and then allowed to drain leaving a residual of liquid within the soil. The column had been weighed previously and was then weighed subsequently to determine the amount of hexane remaining in the soil. An air flow rate of 1.32 L.cm^{-2}. hr^{-1} was introduced into the base of the column and the exhaust gas flow rate and hexane concentrations were measured. The data presented in Figure 13 were collected and show that the saturated concentration of hexane vapour in air (19% v/v) was reached in the exhaust gas in about 30 minutes. It remained at that value until approximately 60 minutes at which time the concentration reduced quickly to near zero. Subsequent weighing confirmed that nearly 100% of the hexane had been recovered.

Because of the vapourization of liquid hexane, the exhaust gas flow rate was significantly greater than the inlet air flow rate. The pressure drop across the column reduced from approximately 1.5 kPa at the start to 1.3 kPa at the end due likely to the increased gas conductivity as the liquid hexane was removed from the soil pores.

In a subsequent experiment, the air flow rate was reduced by one-half to 0.66 L.cm^{-2}. hr^{-1}. The exhaust gas vapour concentration reached saturation at about the same time but remained there for twice as long as the previous experiment and then dropped to zero abruptly.

The trend observed in this experiment where the exhaust vapour concentration builds up to saturation and stays there until depletion, is consistent with expectations in the design of field systems. In these experiments all the air supplied passed through the zone of contamination. In many field cases, however, it is likely that a substantial portion of the induced air flow will by-pass the zone of contamination. In these cases, it is therefore not possible to predict the exhaust gas vapour concentration, the time required to vent the zone and the recovery efficiency.

2. Hexane Residual as a Cylindrical Slug Within the Soil

In these experiments, hexane was introduced into the column through a smaller diameter brass tube and allowed to drain creating a cylindrical slug of hexane with the soil. The cylinder was weighed to determine the mass of hexane remaining. Forced air was then passed upward through the column in a direction along the axis of the slug (and the column). Inlet and outlet gas flow rates and pressure differentials across the column were measured.

The results of five experiments are shown in Figures 14 and 15. The mass of hexane in the experiments was 20, 30 or 40 g and the inlet air flow rate was 0.75 or 1.5 L.cm^{-2}. hr^{-1}. In these experiments, the total inlet air flow did not pass through the zone of contamination and, as was expected, the exhaust gas was not saturated with hexane.

The data in Figure 14 also show that the exhaust gas concentration depends on both the mass of hexane present in the soil and the air flux rate. The highest concentrations occurred with the highest initial liquid hexane concentration (40 g) and the lowest air flux rate (0.75 $L.cm^{-2}.\ hr^{-1}$). Conversely, the lowest concentration occurred with the lowest initial liquid hexane concentration (30 g) and the highest air flux rate (1.50 $L.cm^{-2}.\ hr^{-1}$). However, the time required to strip the hexane completely reduced with increased air flux rate.

Figure 15 shows that the rate of hexane removal increased with increased air flux rate and was independent of initial hexane concentration at the 30 and 40 g levels. At the 20 g initial hexane level but at an equivalent air flux rate, the rate of hexane removal became dependent upon the initial hexane level.

In all experiments, in excess of 95% recovery of hexane was experienced.

3. Comment

The results of the forced air venting experiments are only preliminary but certain important trends are evident at this time. The most important is that the assumption of saturated vapour concentrations in the exhaust gas at a site where forced air venting is used is not justified unless all the air passes through the zone of contamination. This is unlikely to be the case in most field applications. The results to date have also shown that the exhaust gas vapour concentration and the time to achieve complete removal depend heavily on the air flow rate, the mass of contaminant spilled and the geometry of the spill. It is anticipated that further experimentation will allow these dependencies to be quantified for use in system design.

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Table 1 Vapour and Soil Parameters Used in Simulations

Viscosities (μ, Pa.S)

Methane	Pentane	Acetone	Air
1.05×10^{-5}	6.7×10^{-6}	7.3×10^{-6}	1.8×10^{-5}

Effective Diffusion Coefficients (D_e, m.^{2} s^{-1})

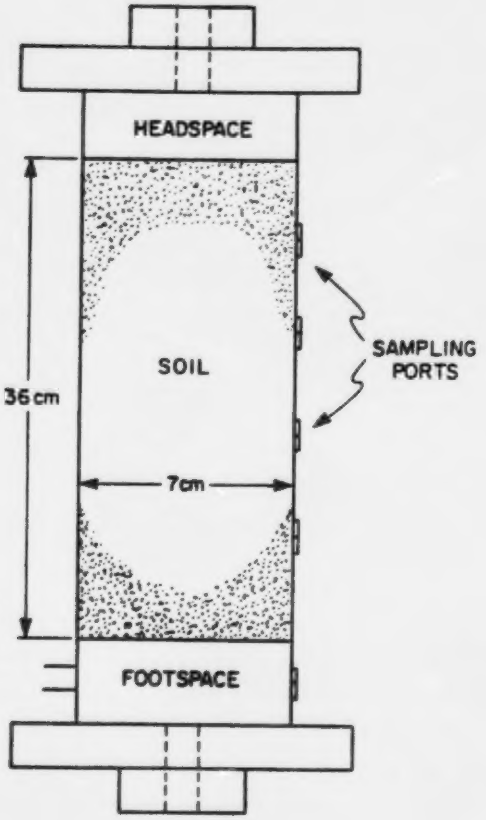
Methane	Pentane	Acetone
1.7×10^{-5}	7.1×10^{-6}	1.3×10^{-5}

Soil Properties (Uniform Sand)

ε (air filled porosity) = 0.35
K_x and K_z (intrinsic permeability) = 1.45×10^{-11} m^2
$\bar{M}$ (moisture content) < 1% w/w

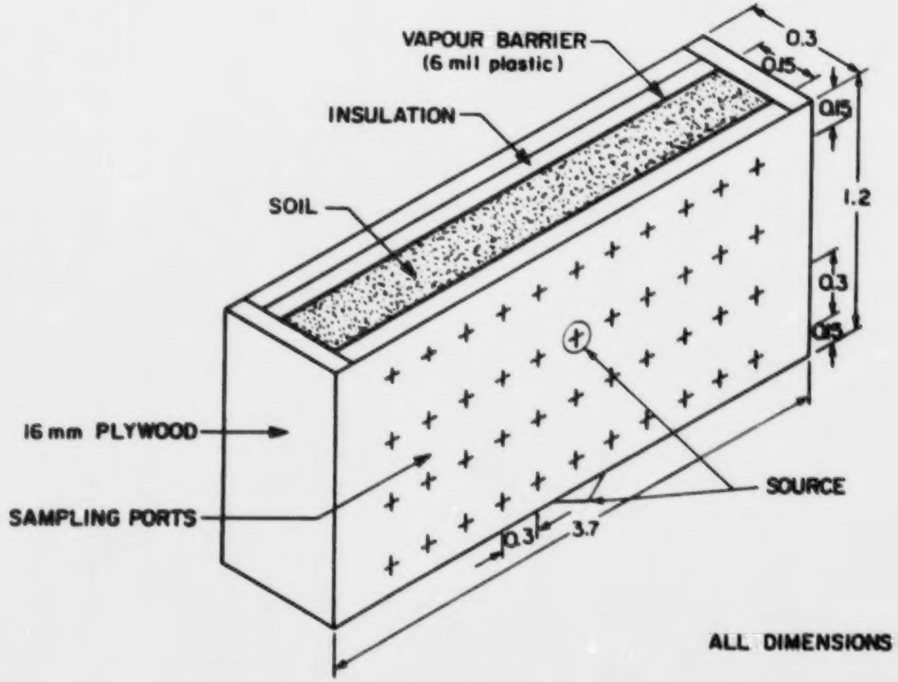
FIGURE CAPTIONS

Figure No.	Caption
1	1-D vapour flux column with source space at the top and bottom
2	2-D vapour flux chamber with source additions at the or suspended in the soil
3	Downward flux of acetone vapours through dry sand: upper, experimental data; lower, simulations
4	Upward flux of acetone vapours through dry sand: upper, experimental data; lower, simulations
5	Acetone vapour flux in 2-D chamber from bottom source after 95 hours: upper, data; lower, simulations
6	Pentane vapour flux in 2-D chamber from bottom source after 24 hours: upper, data; lower, simulations
7	Pentane vapour flux in 2-D chamber from bottom sources after 72 hours: upper, data; lower, simulations
8	Pentane vapour flux in 2-D chamber from suspended source after 12 hours: upper, data; lower, simulations
9	Pentane vapour flux in 2-D chamber from suspended source after 72 hours: upper, data; lower, simulations
10	Apparatus used to measure vapour adsorption onto soil
11	Isotherms for acetone adsorption onto dry clay and sand soils
12	Isotherms for trichloroethylene (TCE) onto dry soils
13	Hexane vapour concentrations in gas exhausted from soil during 1-D forced air venting experiments: source as residual hexane across the base of the soil
14	Hexane vapour concentrations in gas exhausted from soil during 1-D forced air venting experiments: source as residual hexane in a slug within the column
15	Cumulative mass of hexane exhausted from 1-D forced air venting experiments: source as residual hexane in a slug within the column


HEADSPACE
SOIL
SAMPLING PORTS
36cm
7cm
FOOTSPACE

1-D VAPOUR FLUX COLUMN

Figure 1


VAPOUR BARRIER
(6 mil plastic)
INSULATION
SOIL
16 mm PLYWOOD
SAMPLING PORTS
SOURCE
0.3
0.15
0.15
1.2
0.3
0.15
0.3
3.7

ALL DIMENSIONS IN m

2-D VAPOUR FLUX CHAMBER

Figure 2

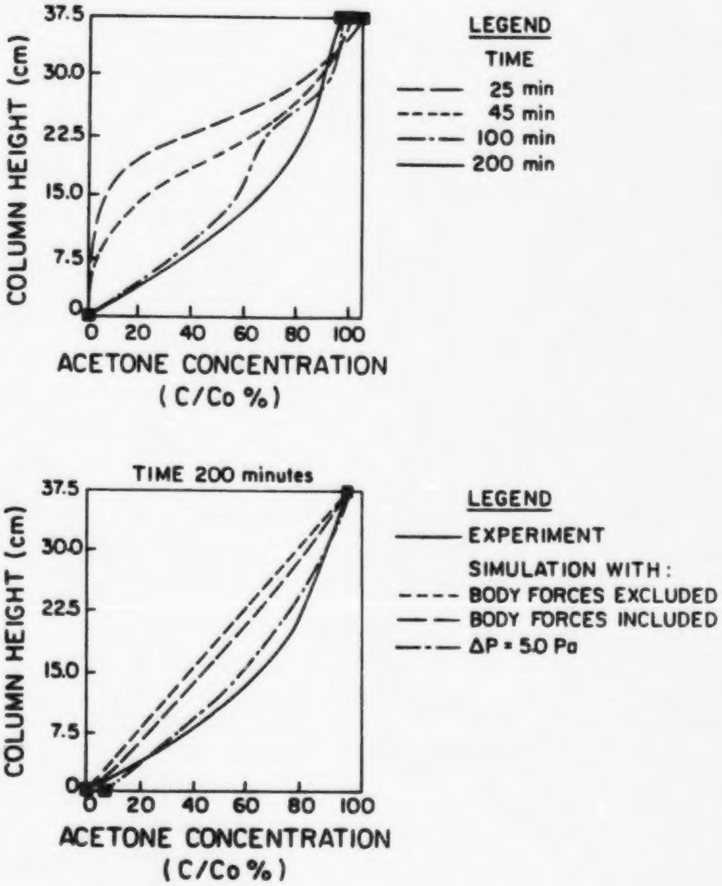

37.5
30.0
22.5
15.0
7.5
0
COLUMN HEIGHT (cm)
0 20 40 60 80 100
ACETONE CONCENTRATION
(C/Co %)
LEGEND
TIME
25 min
45 min
100 min
200 min
TIME 200 minutes
37.5
30.0
22.5
15.0
7.5
0
COLUMN HEIGHT (cm)
0 20 40 60 80 100
ACETONE CONCENTRATION
(C/Co %)
LEGEND
EXPERIMENT
SIMULATION WITH:
BODY FORCES EXCLUDED
BODY FORCES INCLUDED
ΔP = 5.0 Pa

Figure 3

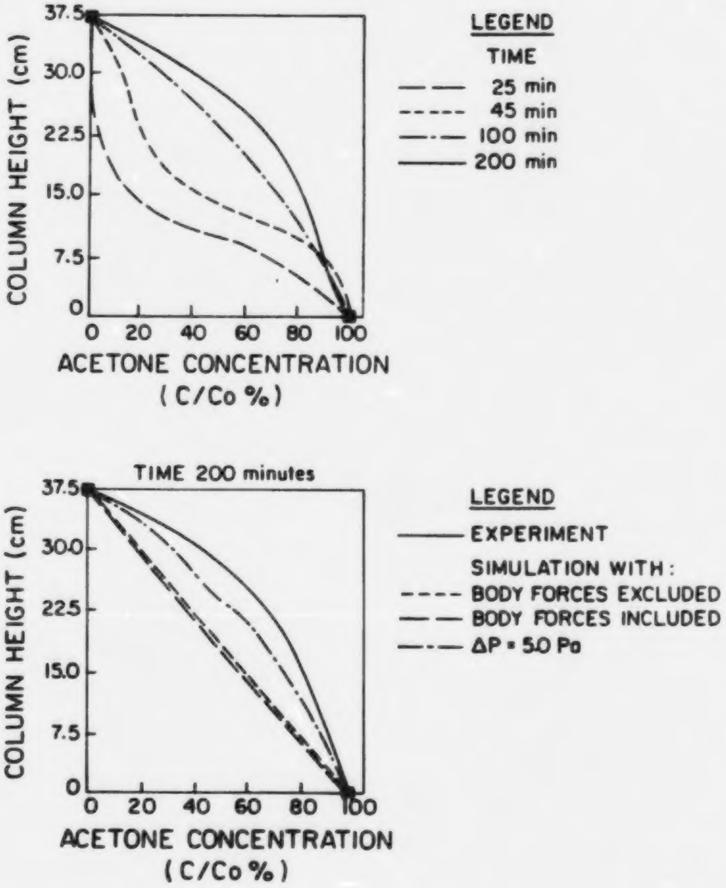
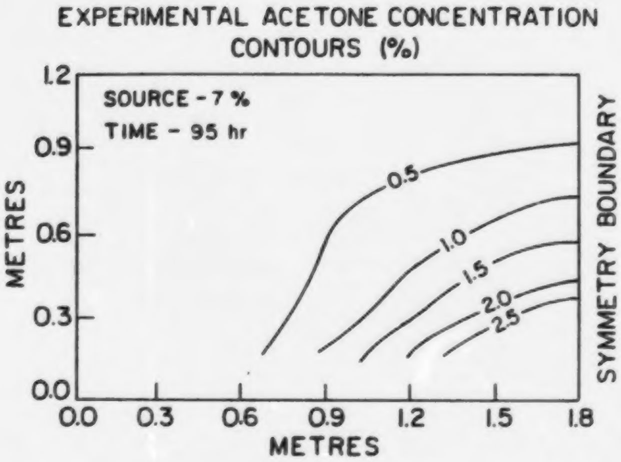
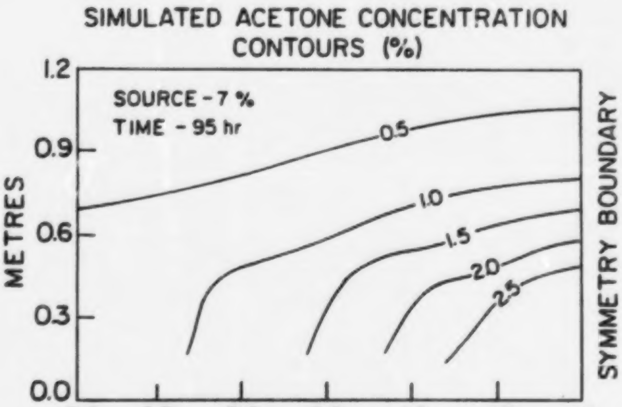

37.5
30.0
22.5
15.0
7.5
0
COLUMN HEIGHT (cm)
0
20
40
60
80
100
ACETONE CONCENTRATION
(C/Co %)
LEGEND
TIME
— — 25 min
- - - - 45 min
—·— 100 min
—— 200 min
TIME 200 minutes
37.5
30.0
22.5
15.0
7.5
0
COLUMN HEIGHT (cm)
0
20
40
60
80
100
ACETONE CONCENTRATION
(C/Co %)
LEGEND
—— EXPERIMENT
SIMULATION WITH:
- - - - BODY FORCES EXCLUDED
— — BODY FORCES INCLUDED
—·— ΔP = 5.0 Pa

Figure 4

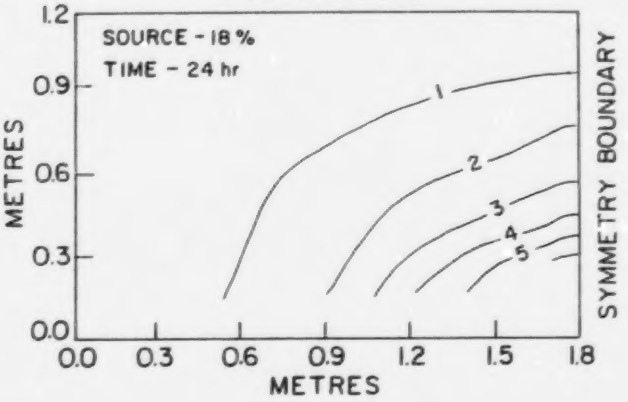


EXPERIMENTAL ACETONE CONCENTRATION CONTOURS (%)

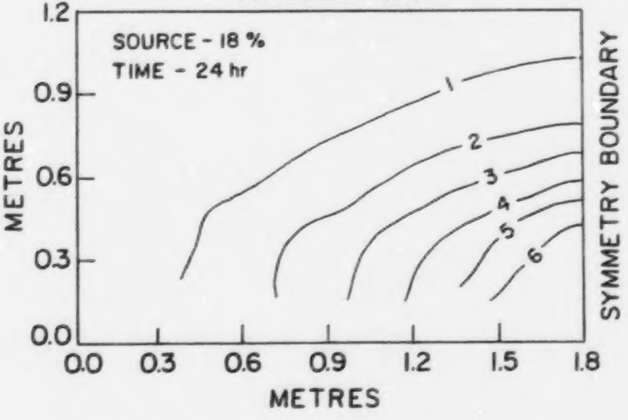


SIMULATED ACETONE CONCENTRATION CONTOURS (%)

Figure 5



EXPERIMENTAL PENTANE CONCENTRATION CONTOURS (%)



SIMULATED PENTANE CONCENTRATION CONTOURS (%)

Figure 6

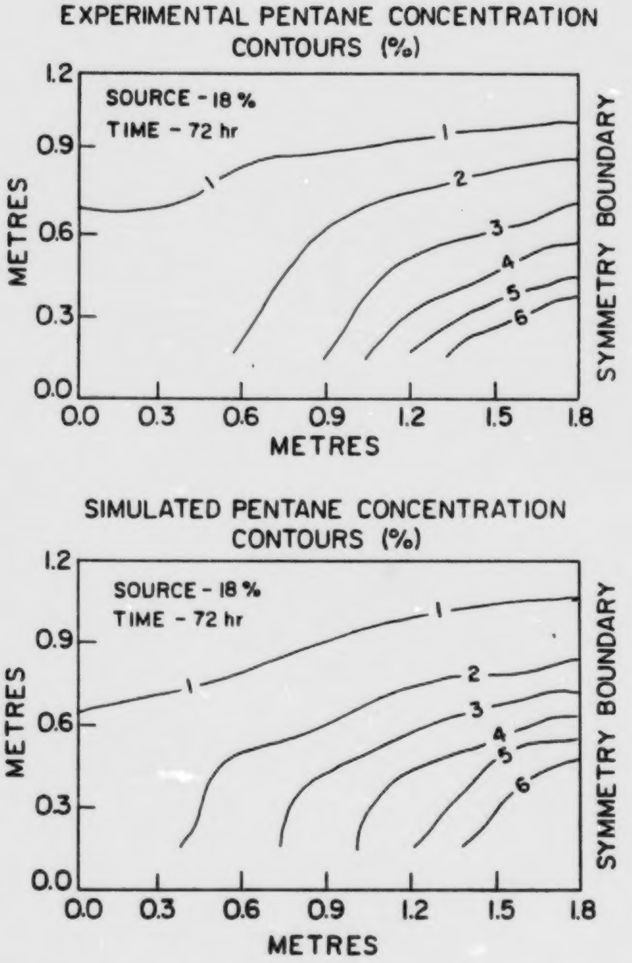

EXPERIMENTAL PENTANE CONCENTRATION CONTOURS (%)
SOURCE - 18 %
TIME - 72 hr
1
1
2
3
4
5
6
1.2
0.9
0.6
0.3
0.0
METRES
0.0
0.3
0.6
0.9
1.2
1.5
1.8
METRES
SYMMETRY BOUNDARY
SIMULATED PENTANE CONCENTRATION CONTOURS (%)
SOURCE - 18 %
TIME - 72 hr
1
1
2
3
4
5
6
1.2
0.9
0.6
0.3
0.0
METRES
0.0
0.3
0.6
0.9
1.2
1.5
1.8
METRES
SYMMETRY BOUNDARY

Figure 7

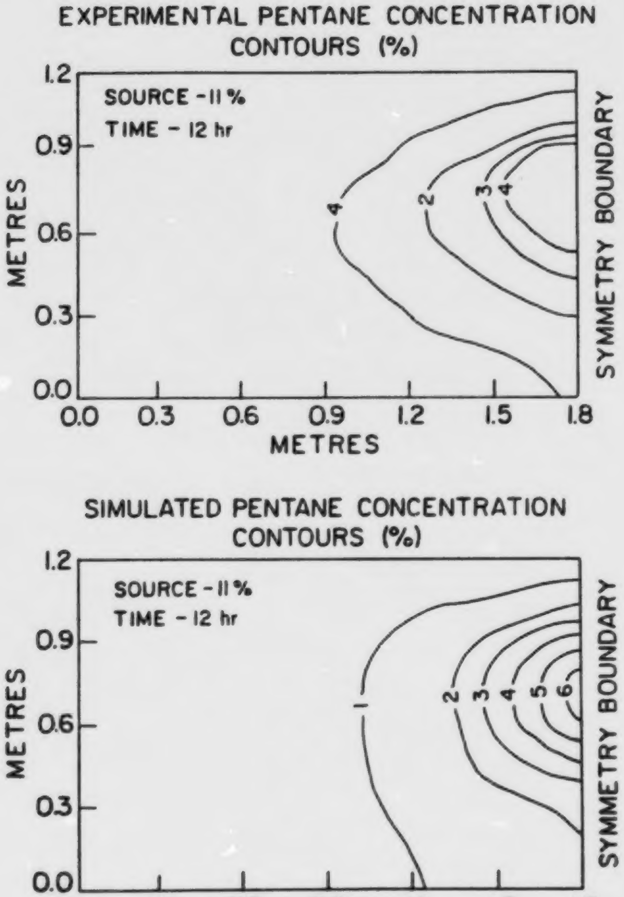
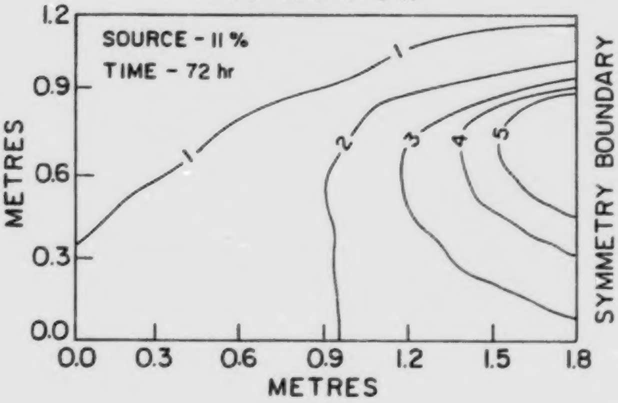

EXPERIMENTAL PENTANE CONCENTRATION CONTOURS (%)
SOURCE - 11 %
TIME - 12 hr
METRES
1.2
0.9
0.6
0.3
0.0
4
2
3
4
SYMMETRY BOUNDARY
0.0
0.3
0.6
0.9
1.2
1.5
1.8
METRES
SIMULATED PENTANE CONCENTRATION CONTOURS (%)
SOURCE - 11 %
TIME - 12 hr
METRES
1.2
0.9
0.6
0.3
0.0
1
2
3
4
5
6
SYMMETRY BOUNDARY
0.0
0.3
0.6
0.9
1.2
1.5
1.8
METRES

Figure 8

EXPERIMENTAL PENTANE CONCENTRATION CONTOURS (%)



SIMULATED PENTANE CONCENTRATION CONTOURS (%)

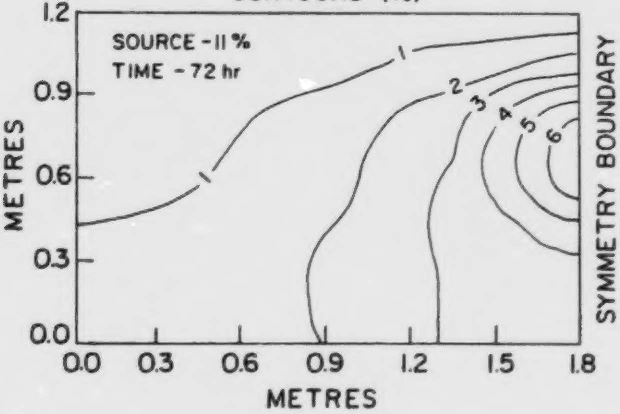


Figure 9

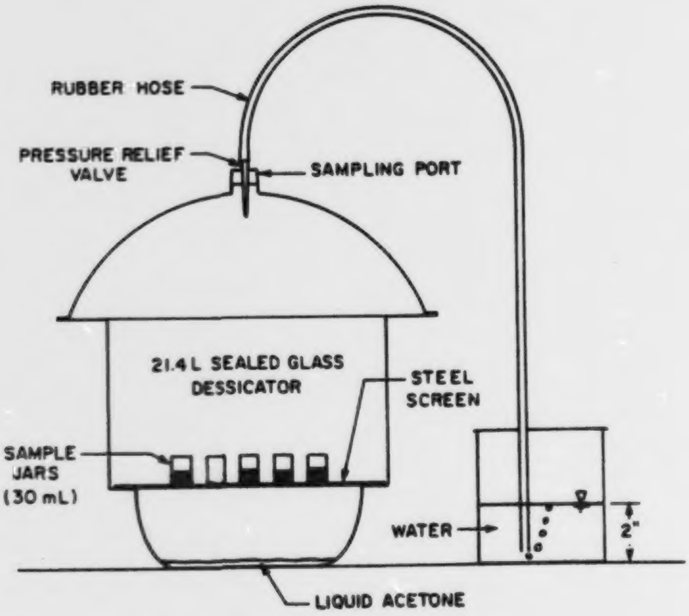

RUBBER HOSE
PRESSURE RELIEF VALVE
SAMPLING PORT
21.4 L SEALED GLASS DESSICATOR
STEEL SCREEN
SAMPLE JARS (30 mL)
WATER
2"
LIQUID ACETONE

Figure 10

DETERMINATION OF FREUNDLICH CONSTANTS FOR ACETONE ADSORBING ONTO TWO SOILS

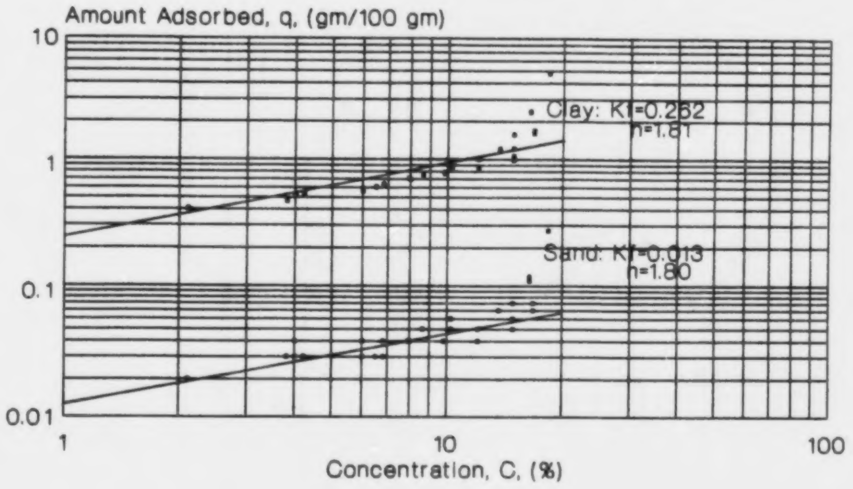


Figure 11

DETERMINATION OF FREUNDLICH CONSTANTS
FOR TCE ADSORBING ONTO CLAY

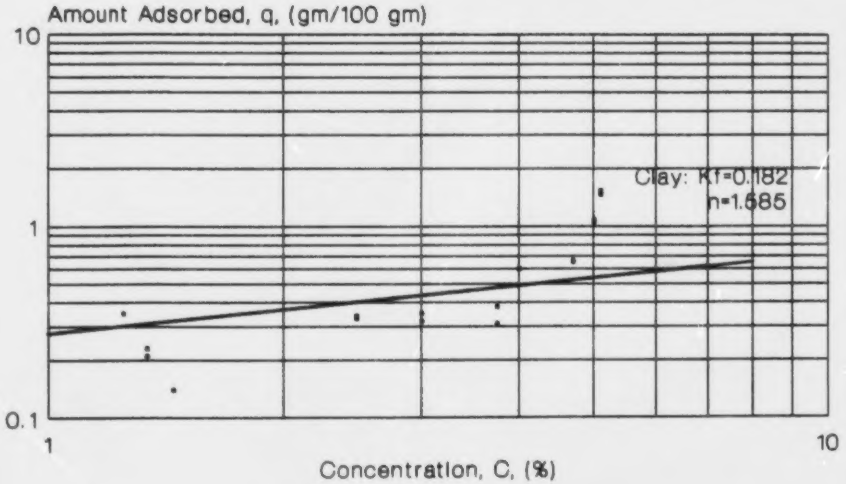
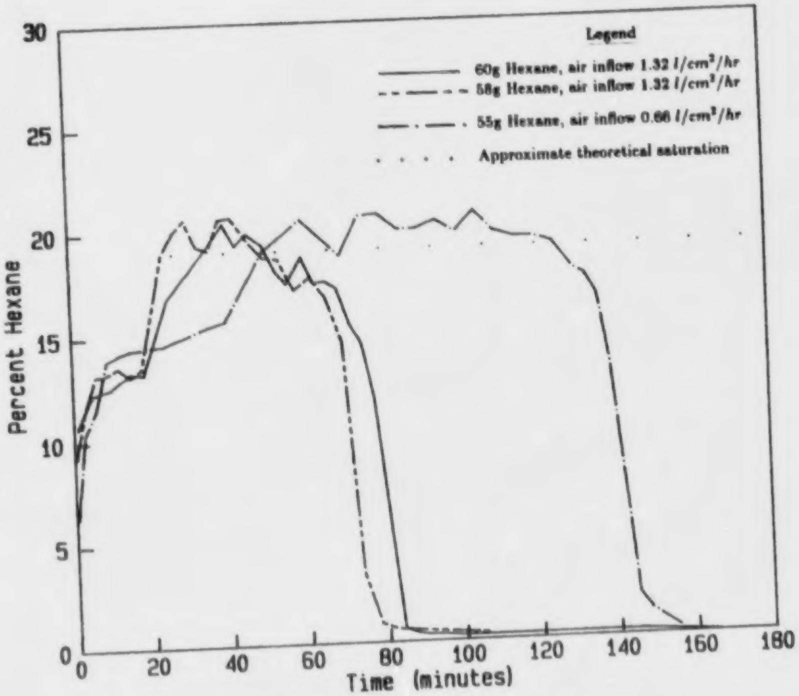
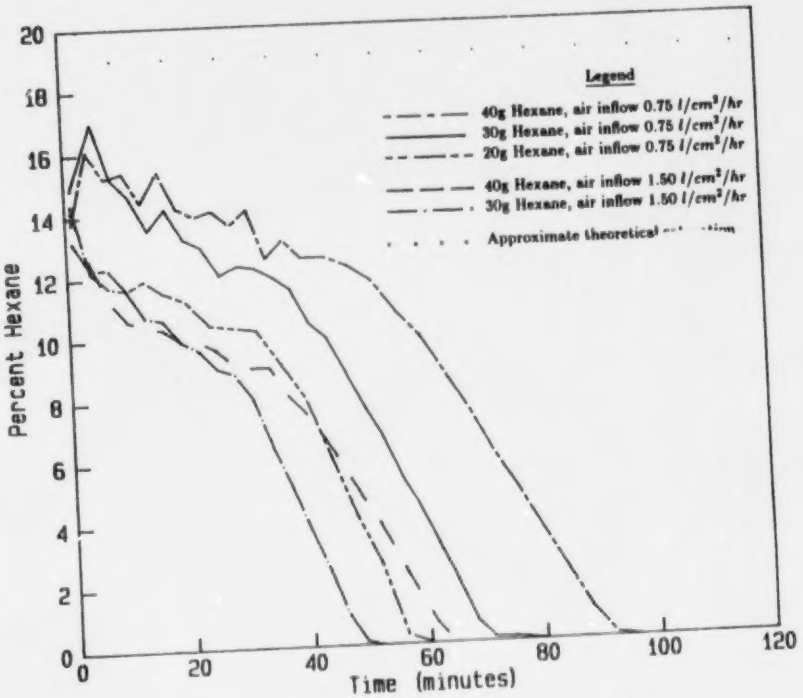


Figure 12



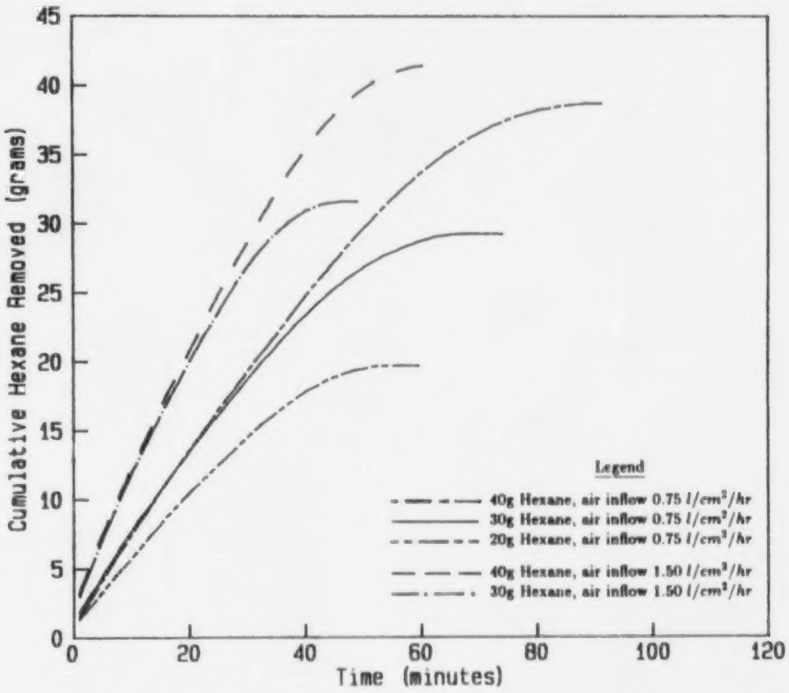
PERCENT HEXANE IN EXHAUST VAPOUR
(bottom portion of column at residual saturation)

Figure 13



PERCENT HEXANE IN EXHAUST VAPOUR
(5 cm diameter cylindrical plug)

Figure 14



CUMULATIVE HEXANE IN EXHAUST VAPOUR
(5 cm diameter cylindrical plug)

Figure 15

C3

EFFECTS OF INCREASING AMOUNTS OF NON-POLAR ORGANIC LIQUIDS IN DOMESTIC WASTE LEACHATE ON THE HYDRAULIC CONDUCTIVITY OF CLAY LINERS IN SOUTHERN ONTARIO

F. Fernandez and R.M. Quigley
Geotechnical Research Centre
Faculty of Engineering Science
The University of Western Ontario
London, Canada, N6A 5B9

ABSTRACT

The results of a three-year research study of the effects of organic liquids on the integrity of southern Ontario clayey soils used as barriers below sanitary landfills are summarized. Concentrated organic solvents (> 70%) such as dioxane and ethanol produce spectacular (up to 1000-fold) increases in the hydraulic conductivity of clays at low effective stresses. Below 70% concentration, the viscosity of leachates containing dioxane or ethanol doubles or even triples that of normal leachate, resulting in significant decreases in k. At the higher concentrations, entry of the low dielectric constant organic liquids into the double layers causes their contraction and an increase in free pore space at constant void ratio that overwhelms any viscosity effects.

Tests run at vertical effective stresses of 0, 40, 80 and 160 kPa show that the presence of effective stresses on the samples during permeation greatly reduces, or even prevents, the above noted increases in k for $\sigma'_v = 0$. For all ethanol/leachate mixtures application of $\sigma'_v = 40$ kPa prevented any increase in k. For high concentrations of dioxane in leachate, however, much higher stresses are required.

Effective stress application subsequent to the large increases in k produced by the concentrated dioxane permeation at $\sigma'_v = 0$ failed to improve the soil. It appears the stresses must be in place on the water-compacted clay in order to effect chemical consolidation during dioxane permeation.

INTRODUCTION

This paper summarizes the results of a three-year research study on the effects of organic liquids in domestic waste leachate on the hydraulic conductivity, k, of southern Ontario clayey soils. Previous papers presented in the proceedings of the 6th, 7th and 8th Technology Transfer Conferences (Quigley and Fernandez, 1985; Quigley et al, 1986; and Quigley and Fernandez, 1987) detail the progress of the study.

The hydraulic conductivity of southern Ontario's surface clays compacted with water can be dramatically increased by permeation of concentrated organic liquids (Fernandez and Quigley, 1985), whereas domestic waste leachate (by itself) shows little effect on k. The laboratory testing completed by the second year of the project led to the conclusion that leachate/hydrocarbon mixtures (ethanol and dioxane) have little effect on k at organic liquid contents below ~ 70%.

The third year of the study has been aimed at: 1) evaluating the effect of leachate/hydrocarbon mixtures on k for undisturbed samples of grey, unweathered clays from Sarnia; and 2) determination of the magnitude of effective stresses required on the brown clays to prevent the large increases in k for highly concentrated organics.

MATERIALS

The soils studied are considered to be representative of candidate soils for natural or compacted hydraulic barriers beneath waste disposal sites. The majority of the testing was done on a soil from the brown surface crust of a thick clay deposit near Sarnia in southwestern Ontario. Selected tests were extended to deeper samples of grey, less weathered clayey soils also from near Sarnia. The permeants used include domestic landfill leachate and hydrocarbon liquids considered to represent the extremes of soluble chemical industrial waste.

The domestic leachate was obtained from the Westminster Sanitary Landfill, City of London, Ontario, and is considered to be representative of raw domestic waste leachate. The fresh leachate is a clear grey liquid of pungent odour and has a salinity of ~ 5 g/L.

Dielectric constant and kinematic viscosities of aqueous solutions of methanol, ethanol, acetone and dioxane are presented on Figure 1. The dielectric constants of the aqueous solutions (Figure 1b) show a steady proportional decrease with hydrocarbon content, from ~ 78 for pure water to the values for each concentrated solvent. The addition of methanol, ethanol, acetone or dioxane to water increases the kinematic viscosity up to a maximum as shown by the curves on Figure 1a. The maximum values surpass the viscosity of pure water by a factor ranging from ~ 1.5 (acetone) to ~ 3 (ethanol). Beyond the maxima, the viscosities decrease to values typical of the concentrated solvents.

Dioxane and ethanol were selected as representative extremes of water-soluble hydrocarbons for the present study.

PERMEANT COMPACTED CLAYS

Hydraulic conductivity testing of clays mixed and compacted with subsequent permeants has the apparent advantage that the soil is in "chemical equilibrium" with the permeant from the start of testing. This considerably reduces permeation times and is occasionally advocated as a suitable procedure for studies of clay/leachate compatibility. Since the soils are thoroughly mixed with the permeants, maximum permeant control on the soil fabric (normally flocculation) is produced during sample preparation. If properly interpreted, this type of testing can yield useful information on the behaviour of clay/organic liquid systems. However, it must be borne in mind that a water-compacted clay will normally have a much more dispersed initial fabric.

Figure 2a shows the results of two sets of k tests for brown Sarnia clay moulded and permeated with water/ethanol mixtures at void ratios of 0.8 and 1.2. For both cases, slight decreases in k were observed in the low to moderate ethanol concentration range. The corresponding data, corrected for viscosity effects, are shown on Figure 2b as intrinsic permeability, K. Both curves show steady increases in K with increasing hydrocarbon content throughout the whole range of ethanol concentrations. This suggests that the decreases in k are due to higher permeant viscosities (Figure 1a) in the 10 to 50% ethanol range. The rate of increase in K (as indicated by the slope of the dashed lines) is significantly higher in the high ethanol concentration range (> 50%).

Control tests carried out on reference kaolinite and montmorillonite clays are shown on Figure 3a relative to the brown Sarnia clay at a void ratio of 0.8. Kaolinite exhibits values of k that are mainly controlled by the viscosity of the permeant. This seems confirmed by only very slight increases in intrinsic permeability for the range of ethanol contents (not shown). Montmorillonite, on the other hand, shows some viscosity control on k for ethanol contents of up to 35%, followed by a spectacular 4 orders of magnitude increase in k with increasing alcohol content.

Dioxane/water mixtures showed very pronounced double layer/fabric effects relative to the ethanol/water mixtures, as shown on Figure 3b. The open, highly flocculated fabric created by all of the dioxane/water solutions swamped any viscosity effects and k increases for the entire range of dioxane contents.

WATER SATURATED CLAYS (COMPACTED OR UNDISTURBED)

In this section, all results described pertain to water-compacted clays except for the grey clays from 11 m depth which were taken from Shelby tube samples and tested undisturbed.

Figure 4a shows the hydraulic conductivity test results at zero static effective stresses for samples permeated with leachate containing 0, 20, 40, 60, 80 and 100% ethanol. Reference values for water used as the initial permeant (circles) are shown along with the final equilibrium values for the organic permeants (triangles). The figure shows that significant decreases in k occurred for ethanol contents of up to 60%. The sample permeated with 80% ethanol doubled the k value for water and concentrated ethanol increased k by a factor of more than 100. The decreases in k observed in the "dilute" concentration range are directly related to the increased viscosity of the permeant.

The values of hydraulic conductivity for samples permeated with domestic waste leachate containing non-polar dioxane (10, 20, 40, 70, 85 and 100%) are shown on Figure 4b. The permeants containing up to 70% dioxane produced viscosity related decreases in **k**, whereas increases in **k** of 2 and 3 orders of magnitude were produced by 85% and 100% dioxane, respectively. The spectacular increases in **k** for the samples permeated with 85 and 100% dioxane are evidence of double layer contraction in the high concentration range. Thorough summaries of this work are presented by Quigley and Fernandez, 1987 and Fernandez and Quigley, 1988.

The results of a series of four hydraulic conductivity tests run on undisturbed samples of grey Sarnia clay at a moisture content of ~ 20.5% are summarized on Figure 5.

Permeation with 0.01 N $CaSO_4$ (reference water) for ~ 2 pore volumes yielded values of **k** ranging from 1.3×10^{-8} to 1.8×10^{-8} cm/s. The samples were then permeated with leachate/ethanol mixtures containing 0, 40, 80 and 100% alcohol.

The interpretation shown on Figure 5a shows significant, viscosity related, decreases in **k** taking place for ethanol contents of up to 70% followed by a small increase at > 70% ethanol. The values of intrinsic permeability (Figure 5b) also increase slightly for high alcohol contents. The increases in **k** for the grey clay are small compared to the more than 100-fold increases observed on Figure 4a for the brown clay. This is a reflection of the lower activity of the unweathered grey clay.

THE IMPORTANCE OF EFFECTIVE STRESSES

The results of hydraulic conductivity tests on water-compacted brown clay samples permeated with leachate/ethanol mixtures under static effective stresses of 160 kPa are summarized on Figure 6a. The static effective stresses appear to compensate for the effects of a lower dielectric constant preventing any increase in k. In fact, the values of k show substantial decreases due to the high viscosity of the organic permeants and chemically-induced consolidation discussed later. Figure 6b shows that the corresponding values of intrinsic permeability, K, are practically unchanged by the leachate/ethanol mixtures.

Figure 7a shows in summary that permeation of water-compacted brown clay at σ'_v = 160 kPa with leachate/dioxane mixtures resulted in only small increases in k at high dioxane contents (compare with Figure 4b). The applied stresses also greatly inhibit the large increases in K noted at σ'_v = 0 kPa (compare Figure 7b and Figure 9b in Quigley and Fernandez, 1987).

Tables 1 and 2 summarize the changes in volume exhibited by the clay samples in response to static effective stresses and seepage stresses generated during permeation. The data in Table 1 show that both the in-place vertical stresses and the seepage drag stresses produced significant consolidation of the sample during permeation of mixtures containing high ethanol contents. For example, at σ'_v = 160 kPa the total settlement equals 1.464 mm for samples originally 20 mm thick (7.3%). The vertical consolidation and K_o effects appear to close any macropores or shrinkage cracks preventing the large increases in k. In Table 2, the data show that samples permeated with leachate/dioxane mixtures also experienced significant consolidation (up to 3.9% of the initial sample thickness) under static stresses of 160 kPa, thus reducing by mechanical means any chemically-induced increases in k at high dioxane contents. The changes in void ratio and hydraulic conductivity from the start to the end of permeation are also presented in Tables 1 and 2.

The pore fluid "organic" composition at the end of each test is presented in Table 3. Two general observations can be made. Firstly, the liquid hydrocarbon content of the pore fluid in the sample at the end of testing is lower than influent permeants. Since the effluent and influent percentages of "organics" are similar, this fact is interpreted to reflect exclusion of organics from the cation-laden double layers of water. Secondly, effective stresses in place on samples permeated with highly concentrated organics seem to have increased the degree of water removal from the pore fluid. It is suggested that the applied stresses prevent macropore development, especially along the fixed walls of the permeameter, thus promoting more uniform flow through the soil mass, and more displacement of the resident pore water.

The very important role of effective stresses in minimizing or even preventing increases in k when the brown Sarnia clay is permeated with concentrated ethanol or dioxane is illustrated in summary form on Figure 8. On Figure 8a, the reference k values for ~ 1 pore volume of water permeation (solid circles) decrease from about 6 x 10^{-9} to 2.5 x 10^{-9} as the applied stresses are increased from 0 to 160 kPa. At σ'_v = 0 kPa, subsequent permeation with ethanol produced a 100-fold increase in k to values even larger than the flocculated clay/ethanol mixtures at a similar void ratio. This fact suggests that clay sample shrinkage, macropore development and "leakage" along the sides of the permeameter may be a major cause of the very large values of k occasionally noted with this type of testing. Effective stresses of only 20 to 40 kPa improve the contact between the clay peds and between the soil and the rigid walls of the permeameter due to K_0 effects. Lateral yield probably reduces or even eliminates side wall flow. In such cases, the final values of k after ethanol permeation are lower than the values for water, a feature partly due to the greater viscosity of ethanol (about 80% higher than pure water).

Permeation with pure dioxane resulted in increases in k, with the magnitudes inversely proportional to the applied effective stresses (Figure 8b). Even at $\sigma'_v = 0$ kPa, however, the measured k was still lower by a factor of 10 than that for the flocculated clay/dioxane mixtures.

The amount of consolidation during dioxane permeation was up to 3% of the sample volume so pore closure was obviously important in reducing some increases in k due to double layer contraction. The seepage drag stresses developed during permeation with ethanol were higher than those for dioxane, thus resulting in reductions in sample volumes by up to 5% and more efficient pore closure.

The data in Table 4 illustrate attempts to restore low permeabilities to damaged, water-compacted clay by applying static effective stresses after permeation of dioxane and ethanol. The dioxane data are also plotted on Figure 9. Original water permeation produced a k value of 6.25×10^{-9} cm/s (k_{OW}) followed by a large increase after dioxane permeation to $k_{OD} = 1.35 \times 10^{-6}$ cm/s. Subsequent application of static effective stresses of 40, 80, 120, 160 and 320 kPa resulted in only partial reduction of k. Even at 320 kPa, the hydraulic conductivity (k_{320D}) remained about 65 times greater than that of water (k_{OW}). In the case of ethanol, however, post damage stress application was much more effective with recovery to low water values at about 80 kPa.

Table 4 illustrates that the recovery of low k values involves large settlements totalling about 8% of the initial sample volume for ethanol. The amount of settlement for the dioxane permeated samples was much less, indicating that the dioxane has apparently caused a strengthening of the clay structure, preventing beneficial consolidation.

CONCLUSIONS

The following major conclusions may be drawn from the three-year project:

Water-Compacted Clays

1. At concentrations up to 60%, water-soluble liquid hydrocarbons typified by ethanol ($\epsilon \approx 32$) and dioxane ($\epsilon \approx 2$), cause decreases in hydraulic conductivity due to increases in viscosity.
2. At liquid hydrocarbon concentrations above 60% and effective stresses close to zero, large increases in k occur due to double layer collapse and development of macropores.
3. At static σ'_v values of only 20 to 40 kPa, chemically-induced consolidation eliminates the increases in k for concentrated ethanol.
4. For dioxane, much higher static σ'_v values are required; small increases in k occurring even at $\sigma'_v \approx 160$ kPa.
5. The brown, weathered, near-surface clayey soils of southern Ontario contain up to 15% smectite and are much more reactive to water-soluble liquid hydrocarbons than are the unweathered grey clays.

6. If large increases in k occur at low stresses due to contact with non-polar dioxane, preliminary studies suggest that the clay structure strengthens significantly so that subsequent application of "corrective" effective stresses causes little consolidation and little reduction in k. In other words, the stresses must be on the water-compacted barrier clay before contact with highly reactive liquid hydrocarbons.

Permeant Compacted Clays

1. Mixtures of domestic waste leachate and various hydrocarbon liquids cause flocculation if mixed with clayey soils prior to compaction.
2. The resulting flocculated soil structures may cause significantly higher k values than water-compacted clays.
3. The flocculated soil structures resist consolidation so that application of effective stresses does not improve k as it does for water-compacted clays.
4. Use of contaminated water or leachate as a wetting agent for soil compaction should not be allowed without very careful study of any flocculating effects.

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Table 1. Void Ratio, Settlement and Hydraulic Conductivity of Brown Water-Compacted Clay Permeated with Leachate/Ethanol Mixtures.

σ'_v (kPa)	Ethanol %	Void Ratio e_o	Void Ratio e_f	Settlement (mm) static	Settlement (mm) seepage	k (cm/s) k_o	k (cm/s) k_f
0	0	0.796	0.756	0	0.446	6.1×10^{-9}	4.8×10^{-9}
	20	0.862	0.836	0	0.275	5.4×10^{-9}	3.3×10^{-9}
	40	0.766	0.714	0	0.591	4.6×10^{-9}	1.7×10^{-8}
	60	0.790	0.752	0	0.428	4.9×10^{-9}	3.5×10^{-8}
	80	0.792	0.755	0	0.418	5.0×10^{-9}	1.1×10^{-8}
	100	0.803	0.767	0	0.397	5.95×10^{-9}	6.2×10^{-7}
40	0	0.772	0.734	0.080	0.353	3.7×10^{-9}	3.3×10^{-9}
	40	0.765	0.685	0.116	0.795	3.3×10^{-9}	1.1×10^{-9}
	80	0.766	0.682	0.132	0.820	3.7×10^{-9}	1.35×10^{-9}
	100	0.770	0.682	0.132	0.862	3.6×10^{-9}	1.8×10^{-9}
80	0	0.803	0.725	0.357	0.507	3.6×10^{-9}	3.55×10^{-9}
	40	0.800	0.698	0.329	0.800	3.35×10^{-9}	1.3×10^{-9}
	80	0.800	0.717	0.348	0.922	3.05×10^{-9}	1.4×10^{-8}
	100	0.809	0.692	0.346	0.954	2.6×10^{-9}	1.4×10^{-8}
160	0	0.754	0.682	0.449	0.375	2.9×10^{-9}	2.75×10^{-9}
	40	0.768	0.662	0.473	0.727	2.6×10^{-9}	1.05×10^{-8}
	80	0.768	0.654	0.502	0.784	2.6×10^{-9}	9.5×10^{-10}
	100	0.795	0.664	0.692	0.772	2.25×10^{-9}	1.35×10^{-8}

Table 2. Void Ratio, Settlement and Hydraulic Conductivity of Brown Water-Compacted Clay Permeated with Leachate/Dioxane Mixtures.

σ'_v	Dioxane	Void Ratio		Settlement (mm)		k (cm/s)	
(kPa)	%	e_o	e_f	static	seepage	k_o	k_f
0	0	0.796	0.756	0	0.446	6.1×10^{-9}	4.8×10^{-9}
	10	0.819	0.780	0	0.424	9.2×10^{-9}	6.4×10^{-9}
	20	0.831	0.798	0	0.366	9.0×10^{-9}	6.1×10^{-9}
	40	0.836	0.812	0	0.267	9.2×10^{-9}	4.4×10^{-9}
	70	0.831	0.821	0	0.190	1.0×10^{-8}	6.1×10^{-9}
	85	0.795	0.777	0	0.193	1.05×10^{-8}	4.2×10^{-7}
	100	0.802	0.786	0	0.177	6.25×10^{-9}	1.35×10^{-8}
40	0	0.772	0.734	0.080	0.353	3.7×10^{-9}	3.3×10^{-9}
	40	0.859	0.772	0.265	0.674	4.9×10^{-9}	3.2×10^{-9}
	80	0.845	0.764	0.200	0.674	4.6×10^{-9}	2.8×10^{-9}
	100	0.805	0.744	0.104	0.569	4.95×10^{-9}	3.9×10^{-7}
80	0	0.803	0.725	0.357	0.507	3.6×10^{-9}	3.55×10^{-9}
	40	0.895	0.790	0.511	0.594	5.15×10^{-9}	3.05×10^{-9}
	80	0.896	0.805	0.627	0.503	5.5×10^{-9}	5.2×10^{-9}
	100	0.804	0.731	0.270	0.547	4.2×10^{-9}	1.8×10^{-7}
160	0	0.754	0.682	0.449	0.375	2.9×10^{-9}	2.75×10^{-9}
	40	0.882	0.769	0.725	0.510	3.85×10^{-9}	2.15×10^{-9}
	80	0.884	0.757	0.762	0.635	3.9×10^{-9}	1.9×10^{-9}
	100	0.827	0.755	0.450	0.339	3.9×10^{-9}	8.6×10^{-8}

Table 3. Hydrocarbon Content of Influent Permeant and Pore Fluid at end of Testing.

σ'_v (kPa)	ETHANOL (%)		DIOXANE (%)	
	Permeant	Pore Fluid	Permeant	Pore Fluid
0			10	14
	20	16	20	18
	40	39	40	31
	60	59	70	67
	80	74	85	60
	100	70	100	86
40	40	35	40	35
	80	70	80	72
	100	93	100	90
80	40	38	40	41
	80	80	80	75
	100	80	100	91
160	40	33	40	42
	80	73	80	76
	100	85	100	

Table 4. Hydraulic Conductivity and Settlement Data for Two Tests in which Effective Stresses were applied to Ethanol and Dioxane Damaged Clays.

Static Effective Stress σ'_v (kPa)	Permeant	Hydraulic Conductivity k (cm/s)	Cumulative Settlement (mm)	
			Static	Seepage
0	Water	$k_{OW} = 5.95 \times 10^{-9}$	0	-
	Ethanol	$k_{OE} = 6.2 \times 10^{-7}$	-	0.397
40	Ethanol	$k_{40E} = 3.7 \times 10^{-8}$	0.551	0.587
80	Ethanol	$k_{80E} = 4.0 \times 10^{-9}$	0.669	0.777
120	Ethanol	$k_{120E} = 1.7 \times 10^{-9}$	1.072	1.227
160	Ethanol	$k_{160E} = 1.7 \times 10^{-9}$	1.342	1.405
320	Ethanol	$k_{320E} = 1.5 \times 10^{-9}$	1.542	1.655
0	Water	$k_{OW} = 6.25 \times 10^{-9}$	0	-
	Dioxane	$k_{OD} = 1.35 \times 10^{-6}$	-	0.177
40	Dioxane	$k_{40D} = 7.2 \times 10^{-6}$	0.283	0.288
80	Dioxane	$k_{80D} = 6.0 \times 10^{-6}$	0.419	0.449
120	Dioxane	$k_{120D} = 6.0 \times 10^{-7}$	0.581	0.596
160	Dioxane	$k_{160D} = 9.0 \times 10^{-7}$	0.658	0.662
320	Dioxane	$k_{320D} = 4.0 \times 10^{-7}$	0.933	0.975

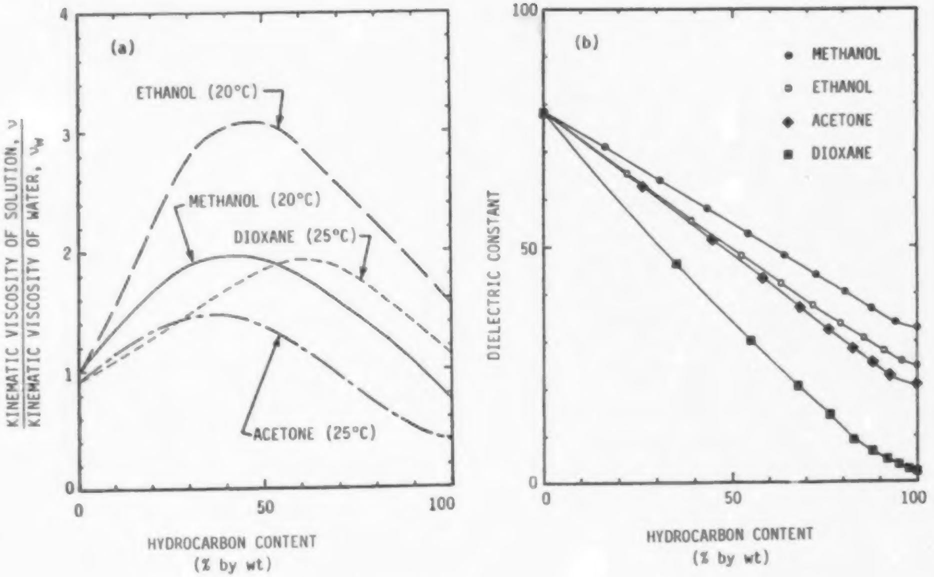
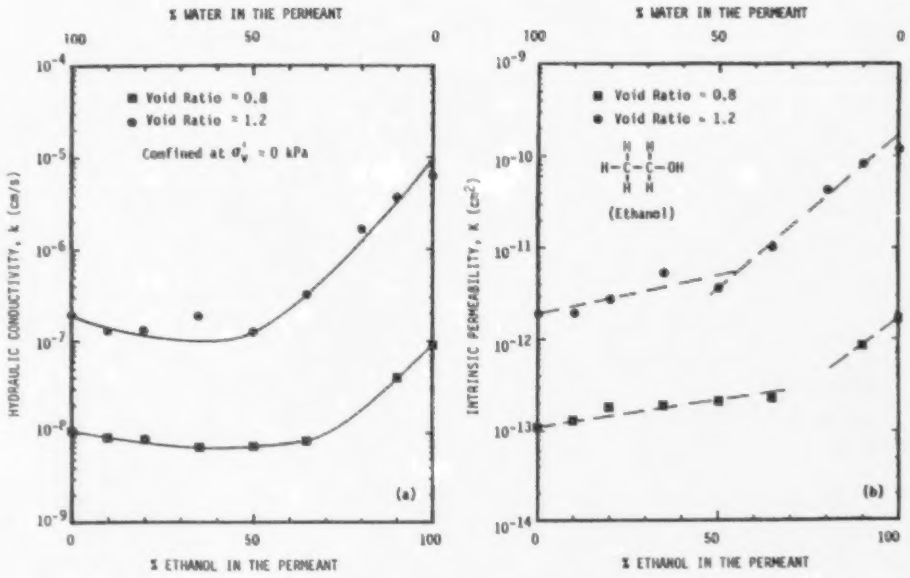


FIGURE 1. PROPERTIES OF WATER HYDROCARBON PERMEANTS: (a) KINEMATIC VISCOSITY; AND (b) DIELECTRIC CONSTANT

Data Sources: Weast, 1984; Flick, 1985; Janz, 1972; Marcus, 1985.



$H-C(H)(H)-C(H)(H)-OH$

FIGURE 2. HYDRAULIC CONDUCTIVITY (a) AND INTRINSIC PERMEABILITY (b) OF BROWN SARNIA CLAY MOULDED, COMPACTED AND PERMEATED WITH WATER/ ETHANOL MIXTURES (Directly from Quigley and Fernandez, 1987)

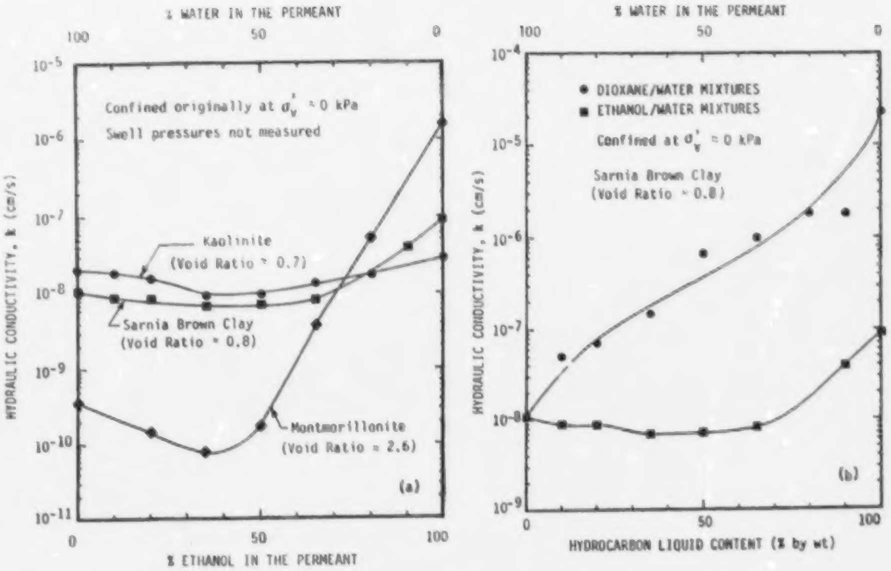


FIGURE 3. HYDRAULIC CONDUCTIVITY OF CLAYS MOULDED, COMPACTED AND PERMEATED WITH AQUEOUS SOLUTIONS OF ETHANOL (a) AND DIOXANE (b) (Adapted from Quigley and Fernandez, 1987)

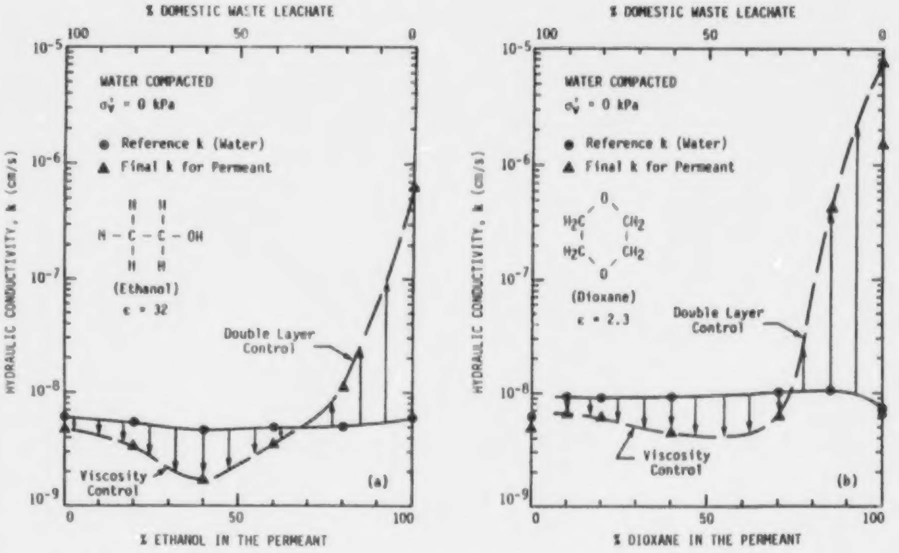


FIGURE 4. HYDRAULIC CONDUCTIVITY OF WATER-COMPACTED BROWN SARNIA CLAY PERMEATED WITH MIXTURES OF (a) LEACHATE/ETHANOL AND (b) LEACHATE/DIOXANE. STATIC EFFECTIVE STRESS, σ'_v = 0 kPa.

(Adapted from Quigley and Fernandez, 1987)

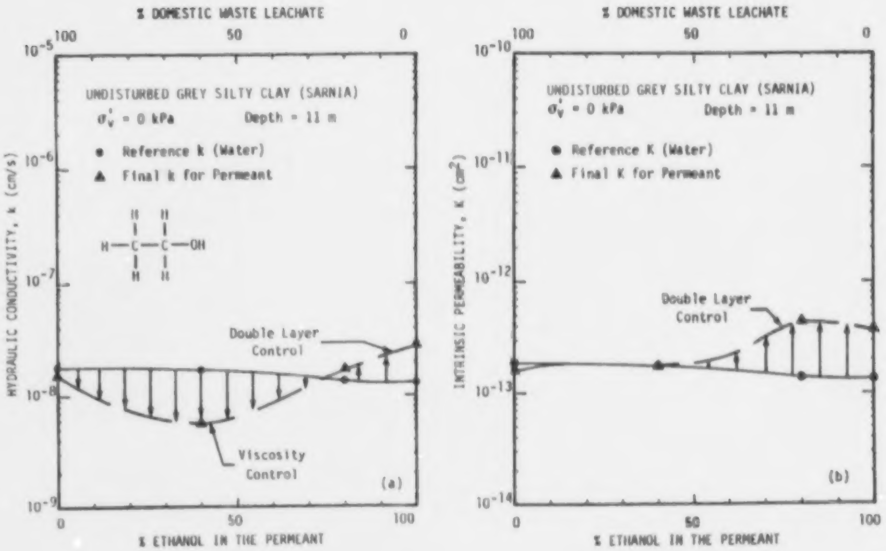


FIGURE 5. HYDRAULIC CONDUCTIVITY (a) AND INTRINSIC PERMEABILITY (b) OF UNDISTURBED GREY SARNIA CLAY PERMEATED WITH LEACHATE/ETHANOL MIXTURES. STATIC EFFECTIVE STRESS, $\sigma_v' = 0$ kPa.

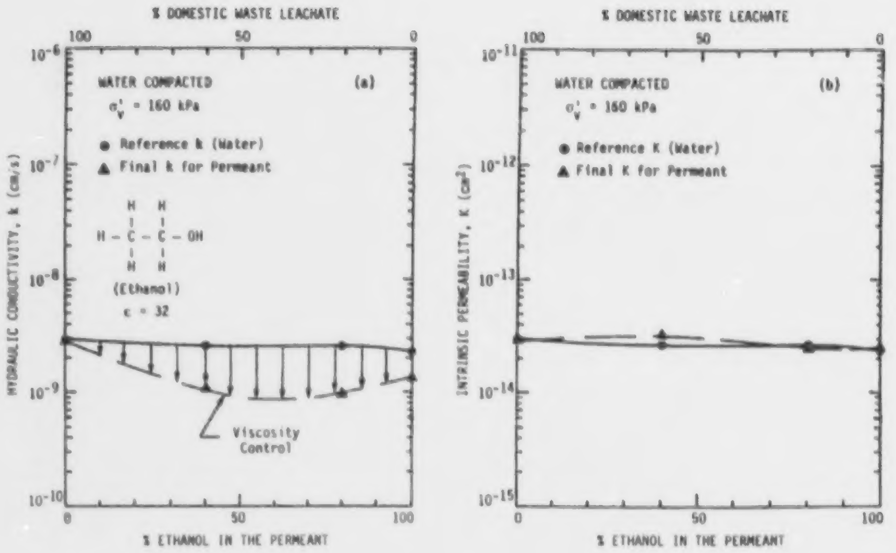


FIGURE 6. HYDRAULIC CONDUCTIVITY (a) AND INTRINSIC PERMEABILITY (b) OF WATER-COMPACTED BROWN SARNIA CLAY PERMEATED WITH LEACHATE/ETHANOL MIXTURES. STATIC EFFECTIVE STRESS, σ'_v = 160 kPa.

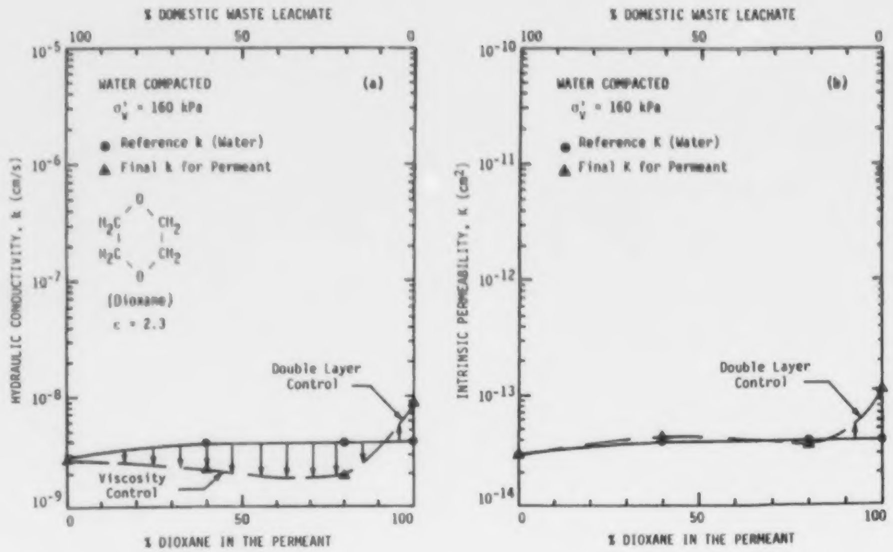


FIGURE 7. HYDRAULIC CONDUCTIVITY (a) AND INTRINSIC PERMEABILITY (b) OF WATER-COMPACTED BROWN SARNIA CLAY PERMEATED WITH LEACHATE/DIOXANE MIXTURES. STATIC EFFECTIVE STRESS, σ'_v = 160 kPa.

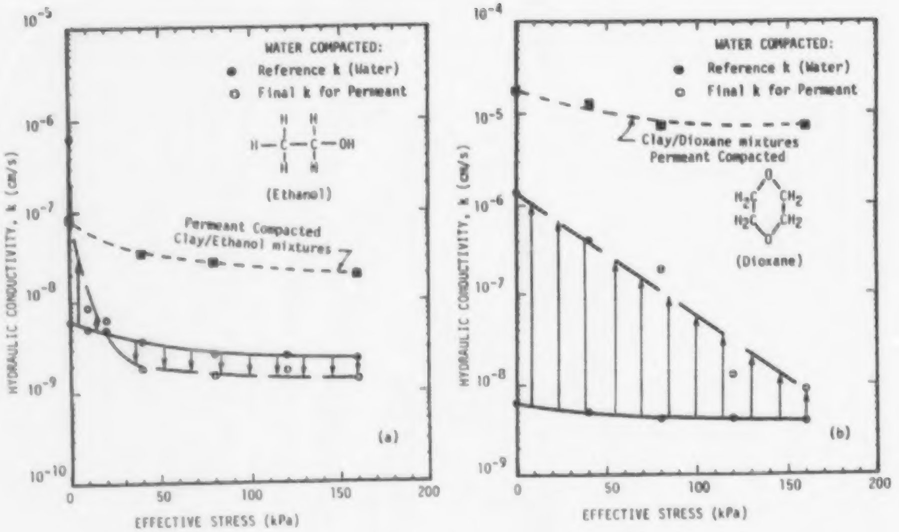


FIGURE 8. COMPARATIVE PLOTS OF HYDRAULIC CONDUCTIVITY VS. CONFINING VERTICAL EFFECTIVE STRESS (a) CONCENTRATED ETHANOL AND (b) PURE DIOXANE. [σ_v' APPLIED TO WATER-COMPACTED CLAY BEFORE LIQUID HYDROCARBON PERMEATION.]

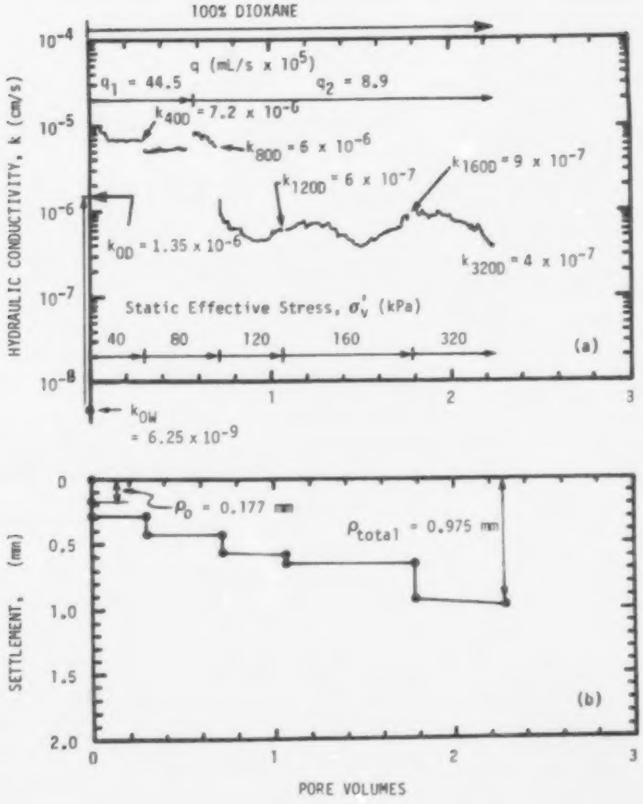


FIGURE 9. DATA VS. PORE VOLUME (TIME) PLOTS: (a) WATER-COMPACTED CLAY PERMEATED WITH CONC. DIOXANE IN STEPS OF INCREASING σ_v'; (b) CORRESPONDING SETTLEMENT STEPS
[k_{40D} = k at 40 kPa, permeant dioxane]

C4

BIOREMEDIATION TECHNOLOGY FOR TREATMENT OF INDUSTRIAL POLLUTANTS: MICROBIOLOGICAL CONSIDERATIONS

Jared Fein and Peter Yu

DIVERSIFIED RESEARCH LABORATORIES LIMITED
1047 Yonge Street
Toronto, Ontario
M4W 2I2

I. ABSTRACT

This paper reviews the current status of bioremediation technology for the detoxification and degradation of hazardous landfill leachates and groundwaters. Microbial biodegradation of numerous industrial pollutants has been well documented in the literature. Physicochemical factors influencing such biodegradations have been identified, leading to the recent development of several processes for hazardous waste bioremediation. Benefits and limitations of this emerging technology will be reviewed. This technology holds considerable promise for future hazardous waste treatment in Ontario and active research in this area should be aggressively pursued and supported.

II. INTRODUCTION

The Ontario Ministry of the Environment (MOE) has identified 41 priority waste disposal sites in 36 municipalities in Ontario, as having potential to negatively impact the surrounding environment (Sibul, 1987). These, as well as numerous other active and inactive sites, are believed to be releasing hazardous materials (Barker *et al.*, 1987; Proulx *et al.*, 1987) into the environment.

Table 1 summarizes data on the compositional variability of hazardous leachates from several Ontario landfill sites. These leachates include many hazardous chemicals including inorganics (halides and metals), alkanes, aromatics, poly-nuclear aromatics and organochlorines. Many of these compounds have been listed as "priority pollutants" by the U.S. Environmental Protection Agency (EPA; Denit, 1984) and by the MOE (MOE, 1982; MISA, 1987). The variability in leachate composition between the different landfills results from many factors, including the characteristics of the particular surrounding industrial base and the nature of the landfill site (soil type, soil structure, pH, etc.).

In response to the requirement for industry to meet new stringent environmental regulations, there has been a tremendous effort in recent years to develop improved waste treatment processes that are both efficient and cost-effective. The purpose of the study we carried out for the MOE was to review recent developments in the field of biological treatment of hazardous wastes, in order to assess their potential applicability for Ontario landfill leachate remediation (Fein and Yu, 1988). The specific objectives of the study were:

(1) To evaluate the feasibility of both traditional and new biological treatment technologies (relative to conventional physical and chemical processes) for hazardous leachate management;

(2) To identify critical process parameters affecting the suitability of biological treatment of hazardous wastes;

(3) To review recent progress in the development of specialized commercial treatment cultures for industrial pollutant biodegradation, concentrating on natural (i.e. non-genetically engineered) microorganisms;

(4) To provide a risk assessment of biological treatment processes; and

(5) To make recommendations for biological process implementation in Ontario, including timing and identification of research needs.

This paper will focus on the microbiological considerations involved in developing full scale bioremediation processes for waste treatment.

III. OVERVIEW OF BIOREMEDIATION TECHNOLOGY

A variety of aerobic and anaerobic biological waste treatment processes have been employed for years for the treatment of wastes such as sewage and food processing effluents. With the widespread manufacture and use of novel man-made synthetic chemicals (i.e. xenobiotic substances), many of which have been found to be very recalcitrant to conventional microbiological treatments, came the realization that traditional biological processes would have to be refined significantly for the treatment of industrial wastes, landfill leachates and other materials containing hazardous compounds. Significant advances have recently been made in the fields of microbial ecology, metabolism, genetics and bioengineering. This in turn has led to the development and recent introduction of some novel biological treatment processes for xenobiotic wastes.

To date, few full scale installations for the biological treatment of hazardous waste chemicals are operating. Aitken and Irvine (1987) have suggested several reasons for the slow introduction of this technology: (1) the lack of a proven track record as a result of too few full scale operating plants; (2) uncertainty by the regulatory authorities and engineering consultants that these untested systems will consistently meet stringent environmental discharge limits; (3) limitations of laboratory feasibility tests, which are unable to truly duplicate the field environment, to accurately predict full scale field performance. The latter stems largely from our insufficient understanding of the complex microbial ecology involved, and from our incomplete knowledge of the true physicochemical and biological parameters affecting microorganisms in treatment systems.

As a result, Aitken and Irvine point out that many pollution problems that could probably be solved more cheaply and efficiently by biological processes are instead being addressed using the more costly, conventional physical and chemical destruction technologies.

The feasibility of any biological treatment process for handling hazardous environmental pollutants will rely on many non-biological and biological parameters. Effective treatment in any biological treatment process will depend on the ability to provide "suitable" type(s) of microorganisms in the treatment system. The microorganisms must also be maintained in an optimal or satisfactory physiological state to obtain good performance. This will be determined by a host of chemical, physical, nutritional and biological factors which affect microbial growth, survival and metabolic activity (Table 2).

Failure in the past to understand these fundamental ecological principles has impeded the successful development of biological processes for treatment of hazardous wastes. For a particular waste problem, the success of a biological process (i.e. efficiency, kinetics of biodegradation and detoxification, stability, control of undesirable microorganisms, etc.) will depend on how well these factors are understood (and controlled) by the designers and operators of the system.

IV. SURVEY OF BIODEGRADABLE ENVIRONMENTAL POLLUTANTS

A. BIODEGRADABLE ORGANIC POLLUTANTS

Microorganisms have an enormous capacity to degrade natural organic substances, given favourable environmental conditions (Alexander, 1965; Atlas and Bartha, 1987). If microorganisms with the appropriate activities are already present in suitable numbers, biodegradation should begin immediately following the introduction of an organic compound into the environment, or following a short induction period.

The situation with respect to unnatural man-made industrial chemicals, which are being added at a rate of 1,200 chemicals a year to the U.S. EPA's current list of 60,000 industrial chemicals (McCormick, 1985), is more complex. In the environment, such molecules may undergo complete or partial biodegradation or may be entirely recalcitrant to microbiological attack. Also, abiotic forces such as spontaneous chemical breakdown or volatilization can account for partial or complete removal of these compounds (Vogel *et al.*, 1987).

A wealth of laboratory data in the recent scientific literature attests to the fact that many, if not most, xenobiotic chemicals are subject to microbiological attack, given the correct environmental conditions and types of microflora (McCormick, 1985; Johnston and Robinson, 1984). Numerous examples are summarized in Table 3.

The compounds listed in the table include most of the hazardous substances of current environmental concern including industrial chemicals from all of the major groups (halogenated hydrocarbons, polychlorinated biphenyls (PCBs), organic pesticides and herbicides, inorganic pollutants, etc.). From Table 3, it will also be seen that many different types of naturally occurring bacteria are responsible for these diverse activities.

B. RECALCITRANCE OF XENOBIOTIC COMPOUNDS

From a practical consideration, the slow rates of biotransformation and biodegradation for many of the xenobiotic compounds constitute a limitation to the technology. Furthermore, the fact that a xenobiotic compound can be biodegraded in the controlled conditions of the laboratory does not necessarily mean that the same process will occur in a field situation. Conditions are likely to be drastically different in terms of physicochemical, hydrological and biological parameters, compositional complexity and strength of the particular waste, as well as scale of operation (McCormick, 1985; Aitken and Irvine, 1987). If the field conditions are not correct, xenobiotic chemicals may be quite resistant to microbial attack and persist for many years.

The term mineralization is used to describe complete microbiological biodegradation of organic materials to carbon dioxide, water and simple inorganic substances. For many xenobiotics, however, biodegradation is only partial, leading to the production of recalcitrant intermediates which may have lower, higher or similar toxicity to the original chemical (Bartha, 1969; Summers and Silver, 1978; Sundstrom, 1982; Roberts, 1987).

Other factors, in addition to unfavourable environmental conditions, are responsible for biological recalcitrance of many xenobiotic compounds, including:

(1) Unnatural chemical substitutions (e.g. chlorination, highly condensed aromatic rings, unusual bonds, etc.) which make the molecules unreactive (e.g. due to steric hindrance, strong electronegativities of halogen substituents) and/or unrecognizable by microbial enzymes (Steiert and Crawford, 1985);

(2) Failure of the xenobiotic substance to induce the synthesis of catabolic enzyme(s) which would degrade it;

(3) Inability of the xenobiotic substance to enter the microbial cell, due to lack of specific transport proteins (permeases);

(4) Limited bioavailability of the xenobiotic substance to the cell;

Bioavailability can be reduced as a result of immobilization of molecules onto inorganic surfaces (e.g. clay particles) or organic particles through adsorption or ionic interactions. Similarly, with highly lipophilic pollutants such as PCBs and other chlorinated hydrocarbons, solubilization and partitioning of the molecules into biological membranes (e.g. in biological sludge) can restrict their accessibility to microbial catabolic processes (Wierich and Gerike, 1981; Richards and Shieh, 1986; Paris *et al.*, 1977; Johnston and Robinson, 1984).

(5) Severe toxicity of the pollutant or its metabolic intermediates for microorganisms.

The cell membranes of microorganisms can concentrate lipophilic toxicants, leading to a 10 to 1000 fold increase in the concentration of these substances in the cells. In biological wastewater treatments, accumulation of hazardous, poorly metabolized lipophilic pollutants into microbial sludges complicates the downstream handling of the sludge. These sludges must be considered as hazardous and should be disposed of accordingly. When evaluating biotreatability data, the investigator must consider the possibility of bioaccumulation, since this phenomenon can remove lipophilic pollutants from the aqueous assay system. This could lead to an overestimation of the extent and rate of biodegradation unless proper chemical mass balances are conducted (Aitken and Irvine, 1987).

C. SIGNIFICANCE OF MICROBIAL COMMUNITIES IN BIODEGRADATION

Numerous laboratory studies have shown that pure microbial cultures (i.e. single species) can attack and degrade many xenobiotic substances. It is important to realize however that, in both natural ecosystems and full scale waste treatment systems, biodegradation is usually mediated by microbial communities containing different types of microorganisms having many different metabolic capabilities. Pure microbial cultures are rarely encountered in natural environments (Slater and Lovatt, 1984).

Many naturally occurring microbial communities capable of biodegrading various xenobiotic substances have been isolated and characterized (Table 4). In an excellent review on the significance of microbial communities on biodegradation, Slater and Lovatt (1984) point out that individual members of these communities are often much less effective than the community as a whole in their abilities to biodegrade many xenobiotic pollutants. This microbial synergy results in significantly enhanced rates of biodegradation and mineralization or biotransformation of a much wider range of xenobiotics than is possible by any of the single species in a community. The term "consortium" has been introduced to describe a two-membered culture or natural assemblage such as those in Table 4 in which each microorganism derives benefit from the other as a result of their interactions (Brock *et al.*, 1984).

For biological waste treatment processes to operate successfully in the field, stability of the microbial communities is a prime need. Any of a number of critical physicochemical or biological factors (see Table 2) can upset the stability of the community and hence, the efficacy of biodegradation. If these parameters are not properly understood and controlled, costly process failures and shutdowns may result.

A wide variety of microbial interactions can affect the performance of a waste treatment process, including commensalism, mutualism, competition and predation (Atlas and Bartha, 1987). Commensalistic or mutualistic interactions may promote biodegradation processes by a number of mechanisms. Nutritional assistance is one means whereby one member of a microbial community provides another with a required growth nutrient. For example, Jenson (1957), characterized a commensalistic microbial community, enriched from soil, which biodegraded trichloroacetic acid (TCA). The community consisted of three microorganisms, an unidentified bacterium (strain 3C1) which could dechlorinate TCA and use it as a primary carbon and energy source for growth, and two species of *Streptomyces*, which were not able to grow on TCA. Strain 3C1 could not grow in the absence of the *Streptomyces* spp., unless vitamin B_{12} was added. In the natural commensalistic culture growing on TCA, it was concluded that one or both of the *Streptomyces* spp. provided strain 3C1 with the essential vitamin while using substrates other than TCA as their carbon and energy sources.

Other mechanisms for nutritional assistance in mutualistic or commensalistic communities include: (1) increasing the availability of a bound or otherwise inaccessible substrate, for example, by excreting a biosurfactant to release an insoluble pollutant (Banerjee *et al.*, 1983; McCormick, 1985); (2) release of extracellular enzymes whose activities provide readily utilizable substrates from otherwise non-available complex substrates (e.g. glucose from cellulose); and (3) production of utilizable substrates through co-metabolism (discussed below).

The detoxification (through biodegradation or biotransformation) of toxic pollutants in an environment is another important mechanism whereby one member of a mutualistic or commensalistic community can assist another and promote the overall efficacy of biodegradation in a biological treatment process.

D. CO-METABOLISM

Co-metabolism, or fortuitous metabolism as it is sometimes called, is a phenomenon whereby a bacterium is able to partially or totally transform a non-growth substrate (i.e. a specific xenobiotic compound) in the obligate presence of another organic compound which serves as its growth substrate (i.e. carbon and energy source). It is a fortuitous form of metabolism in that the reactions are catalyzed by microbial enzymes which have broad substrate specificity (Johnston and Robinson, 1984).

In the case of partial transformation, the chemical intermediates produced by co-metabolism may be available for consumption as carbon and energy sources by other members of the microbial community. For example, the bacterium *Mycobacterium vaccae* is able to co-metabolize cyclohexane while growing on propane, but cannot assimilate either the cyclohexane its co-metabolic by-product, cyclohexanone (Beam and Perry, 1974). The latter, however, can be used by other bacteria in this commensalistic community, which also cannot utilize the cyclohexane.

Although many laboratory examples of co-metabolism have been reported in the literature, the true extent to which it occurs in nature is not clear (Johnston and Robinson, 1984). It's exploitation has been considered as a possible approach to the *in situ* treatment of pollutants, whereby acclimatized microbial seed cultures would be injected along with a growth substrate into a suitable aquifer system (Jhaveri *et al.*, 1983; Wilson and Ward, 1987). It would appear that this approach is being successfully applied to a number of hazardous waste problems, including a few of the so-called Superfund sites in the United States (A. Bourquin, personal commun.). However, as pointed out by McCarty (cited by Roberts, 1987), the economic feasibility of injecting huge quantities of an energy source (i.e. primary substrate) into the ground must be carefully evaluated for each waste treatment situation. Primary energy sources are required at levels of about 100 to 1000 times greater than that of the pollutants if the latter are to be co-metabolized. Thus, for every kilogram of hazardous chemical to be transformed, 100 to 1000 kg of primary substrate would have to be added to the aquifer. The operating costs for such treatment could be enormous! At a Superfund site in Florida being treated *in situ* by ECOVA Corp., the high content of natural organic compounds in the contaminated soil appears to be providing much of the required organic nutrient for the co-metabolizing bacteria (A. Bourquin, personal commun.)

E. GENETICALLY IMPROVED STRAINS

Microbiologists have shown that, for many recalcitrant pollutants, it is possible to develop genetically improved or acclimatized seed cultures (single or mixed species) having an increased capacity to biodegrade or detoxify these compounds. The rationale behind this work is that, by developing a number of specific superior strains and then mixing and matching them, it may be possible to customize microbial preparations for combating specific hazardous waste problems (Gasner, 1979; McCormick, 1985). In particular penta- and tetra-chlorodibenzodioxins (TCDDs) and their dibenzofuran analogues (TCDFs), PCBs, toxaphenes, Dieldrin/Aldrin, Heptachlor and its epoxide, the Chlordanes, Mirex, Kepone and the hexachlorocyclohexane insecticides, have been identified, as deserving high priority attention for research into improving their biodegradability (Johnston and Robinson, 1984). All are highly toxic and persistent in the environment.

Laboratory methods that have been successfully applied include conventional strain isolation and enrichment (acclimatization and adaptation), classical mutagenesis, plasmid-assisted breeding and genetic engineering (Aitken and Irvine, 1987; Chakrabarty, 1974; Johnson *et al.*, 1985; Johnston and Robinson, 1984; Kellogg *et al.*, 1981; Kilbane *et al.*, 1982; McCormick, 1985; Roberts, 1987; Schlegel and Jannasch, 1967; Steiert and Crawford, 1985; Veldkamp, 1974;). Further discussion of these methods and their application to the development of better degradative microorganisms for bioremediation processes are provided in our full report to MOE (Fein and Yu, 1988).

When developing a suitable seed culture for bioaugmentation, regardless of the approach to be taken, there are a number of physiological properties which need to be considered as targets for possible improvement. Table 5 presents a summary of those traits which are desirable or essential for a worthy commercial seed preparation.

A number of suppliers presently are selling natural or acclimatized bacterial seed preparations which they claim offer superior performance for treating certain types of wastes including greases, phenols or even "dioxin herbicide" (Johnson *et al.*, 1985, Gasner, 1979). In many cases, however, the claims made for these microbial cultures appear to be highly exaggerated, unsubstantiated and scientifically questionable (Johnston and Robinson, 1984).

On the other hand, significant progress has been made over the past fifteen years in the development of microorganisms which exhibit enhanced biodegradative abilities towards specific pollutants. The challenge now is to successfully move the technology out of the laboratory and into the field. As seen in Table 2, to be effective in the field a seed microorganism or mixture of seed microorganisms must display a range of physiological properties. The capacity to degrade a particular pollutant in a bioreactor or field situation will be of limited benefit if the microorganisms are susceptible to the toxic effects of other pollutants that might also be present in the waste. With most hazardous wastes, such as industrial landfill leachates, complexity and high toxicity are often the norm (Johnston and Robinson, 1984; Barker *et al.*, 1987; Roberts, 1987).

Furthermore, in all real world treatment situations, the seed microorganisms must successfully compete with the natural indigenous microflora for available resources (nutrients, attachment sites, space, etc.) if they are to establish themselves and effectively catalyze the desired transformations. This in turn will depend on how well the bacteria in the seed preparation can cope with the particular set of conditions imposed by each waste treatment problem. We are still a long way from achieving this objective. Where commercial seed cultures have been effective, continued performance almost always requires that these preparations be readministered to the treatment system on a repeated basis, to maintain the desired level of activity (Johnson *et al.*, 1985). This constrasts sharply with the more economically desirable "one shot" starter culture approach.

For *in situ* treatments of hazardous waste landfills, this problem is magnified since very few of these parameters can be controlled and because of variation in site geology (soil structure and composition, hydrology, etc.). The most important constraint on biodegradation in soils is thought to be the inaccessibility of the pollutants to the microorganisms, as a result of adsorption and other abiotic factors that were discussed earlier. Furthermore, the conditions in such environments are often extreme for microorganisms, being highly toxic due to high concentrations of toxic metals and halogenated compounds and having an unusually low water activity (Johnston and Robinson, 1984). What works well on one particular waste may not work so well on a similar waste at a different treatment site. With above-the-ground treatment, the problem may be somewhat less severe, as operators can control and optimize many of the critical physicochemical factors. Variability in the xenobiotic composition of the wastes, however, will always be a significant factor limiting universal applications of any specifically developed microbial preparation.

The solution to such complex problems may lie in the development of large libraries of biodegradative microorganisms from which specific mixed cultures could be formulated to suit a particular waste problem (McCormick, 1985). Until more is learned about the ecological aspects of biological waste treatment, this goal will not be realized. Furthermore, such libraries will probably have to be quite large, since bacteria capable of degrading one member of a class of xenobiotic substances (e.g. PCBs, toxaphenes or halobenzoates) are often unable to biodegrade another. For example, with benzoic, *p*-hydroxybenzoic and salicylic acids, which differ only in a single hydroxyl substitution, biodegradation of each is mediated by different strains using distinct catabolic pathways (Johnston and Robinson, 1984).

V. FUTURE OUTLOOK

We have seen that microorganisms have an enormous capacity to biodegrade or transform numerous xenobiotic substances, given the right environmental conditions. As was discussed, many interacting factors will ultimately determine the environmental fate of these compounds. At the applied level, the research and development challenge is how to best exploit microorganisms and transfer the emerging technology from the laboratory environment to full scale operational field processes.

Over the past several years we have seen the introduction of a number of pilot scale and full scale biological treatment systems for remediation of contaminated industrial effluents, landfill leachates and groundwaters. Examples include conventionally designed aerobic (e.g. aeration lagoon, activated sludge, etc.) and anaerobic (e.g. anaerobic sludge blanket reactor, anaerobic filter, etc.) systems, as well as a number of newer process designs (e.g. *in situ*, solid, and slurry-phase soil treatment processes, sequencing batch reactor, the hybrid PACT system, etc.). Some of the latter systems are being currently tested at several heavily contaminated landfills in the United States (i.e. Superfund sites) with apparent success. For further discussion of these various processes including references, the reader is referred to our full report to MOE (Fein and Yu, 1988).

Bioremediation holds considerable promise for hazardous waste treatment, and offers many potential advantages over comparable non-biological treatment technologies in current usage. These biological treatments are often quicker and more cost effective than comparable physicochemical processes in current usage. Bioremediation warrants serious consideration for Ontario industrial pollution problems, both as a stand alone technology and as a unit operation to be used in conjunction with other current technologies. The choice of the most suitable process design for a particular pollution problem can only be determined after thorough feasibility analysis both and in the laboratory and on-site.

VI. ACKNOWLEDGEMENTS

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TABLE 1

CONTAMINANTS FOUND IN LANDFILL LEACHATES[a]

Contaminant	Landfill Sites[b]					
	Borden	Woolwich	North Bay	New Borden	Upper Ottawa Street	Tricil
Aliphatic, aromatic and carboxylic acids	20	> 10,000	> 300	--	> 1000	--
Carbon tetrachloride	< 1	5	< 1	9	p	n.d.
Chloroform	< 1	20	< 1	25	5	n.d.
Trichloroethylene	1	37	2	750	p	n.d.
Trichloroethane	n.d.	7	< 1	90	20	8.44
Tetrachloroethylene	n.d.	2	< 1	< 1	< 1	n.d.
Acetone	< 1	-	6	-	6	-
Tetrahydrofuran	p	-	9	-	200	-
1,4-Dioxane	n.d.	-	< 1	-	p	-

(continued)

TABLE 1 (Cont'd)

CONTAMINANTS FOUND IN LANDFILL LEACHATES

Contaminant	Landfill Sites					
	Borden	Woolwich	North Bay	New Borden	Upper Ottawa Street	Tricil
Benzene	3	70	51	50	60	7920
Toluene	1	7500	60	1400	2600	9520
Xylenes	< 1	700	140	500	3500	-
Ethylbenzene	< 1	1100	64	120	700	3320
Tetramethylbenzene	n.d.	10	250	70	450	-
Chlorobenzene	n.d.	n.d.	105	n.d.	110	-
Dichlorobenzenes	< 1	n.d.	13	n.d.	5	-
Naphthalene	n.d.	50	15	260	p	2350
Phenols	-	1100	10	p	p	-
Benzothiozoles	< 1	30	10	n.d.	p	-
PAH's	-	-	n.d.	-	n.d.	-
Phthalates	< 1	p	110	p	p	-

[a] Source: Barker *et al.*, 1987.

[b] The approximate concentrations (mg/L) of selected organic contaminants found in leachate - contaminated groudwaters at six landfill sites.

p = detected but concentration not estimated

n.d. = not detected

- = not determined

TABLE 2

PHYSICAL, CHEMICAL AND BIOLOGICAL FACTORS INFLUENCING MICROBIAL BIODEGRADATION

I. Physical Parameters

- a) Temperature
- b) Alkalinity/pH
- c) Moisture (Water Activity)
- d) Salinity
- e) Oxygen Availability
- f) Redox (Eh)
- g) Soil Structure and Hydrology
    - i. Pollutant Bioavailability
        - -adsorption/ionic binding
        - -solid/liquid interfaces
        - -pollutant spatial distribution in ecosystem

II. Chemical Parameters

- a) Organic Composition and Strength of the Waste Feedstocks, incl.
    - i. Pollutant Composition
    - ii. Pollutant Complexity
    - iii. Pollutant Concentration
- b) Presence of Toxicants
    - i. Toxic Pollutants
    - ii. Toxic Metabolic Intermediates
    - iii. Heavy Metals
- c) Nutrient Availability
    - i. Nitrogen
        - -carbon:nitrogen balance
    - ii. Macronutrients (magnesium, potassium, phosphorous and sulfur)
    - iii. Micronutrients
        - -trace elements (e.g. iron, zinc and nickel)
        - -essential growth factors (e.g. vitamins, amino acids, etc.)

TABLE 2 (Cont'd)
PHYSICAL, CHEMICAL AND BIOLOGICAL FACTORS INFLUENCING MICROBIAL BIODEGRADATION

III. Biological Factors

- **a) Microbial Interactions**
  - **i. Mutualism, Competition, Predation etc.**
- **b) Seed Cultures (Bioaugmentation)**
  - **i. Dose (Inoculum) Size and Frequency**
- **c) Bioaccumulation Affecting Bioavailability**

TABLE 3

EXAMPLES OF POLLUTANT-DEGRADING MICROORGANISMS AND SUBSTRATES[a]

MICROORGANISM	POLLUTANT(S)
Achromobacter	halogenated hydrocarbons, hydrocarbons, phenoxyacetates, *tert*-butylbenzene
Acinetobacter,	diethyleneglycol, hydrocarbons, PCB
Actinomucor elegans	petroleum
Actinomycetes	petroleum hydrocarbons
Aerobacter aerogenes	benzene
Aeromonas	phenanthrene
Agrobacterium	halogenated hydrocarbons
Alcaligenes	halogenated hydrocarbons, hydrocarbons, linear alkylbenzene sulfonates, PCB, polycyclic aromatics
Arthrobacter	benzene, Diazinon, hydrocarbons, pentachlorophenol, phenoxyacetates, polycyclic aromatics, pulp mill lignins, various phenols
Aspergillus	carbamate, malathion, phenoxyacetates, pulp mill lignins, various phenols
Azotobacter	catechol
Bacillus	aromatics, long-chain alkanes
sphaericus	phenylureas
Beijerinckii	anthracene, biphenyl
Brevibacterium	2,4,5,-T, aromatics, halogenated hydrocarbons, phenanthrene, polycyclic aromatics
Candia tropicallis	PCB
Chaetomium globosum	alachlor
Chlorobium thiosulfatophilum	waste gypsum
Chromobacter	pulp mill lignins, various phenols
Cladosporium	petroleum hydrocarbons
Clostridium	halogenated hydrocarbons

(continued)

TABLE 3 (Cont'd)

EXAMPLES OF POLLUTANT-DEGRADING MICROORGANISMS AND SUBSTRATES[a]

MICROORGANISM	POLLUTANT(S)
Corynebacterium	halogenated hydrocarbons, phenoxyacetates
Cunninghamella elegans	PCB
Desulfobacter postgateii	waste gypsum
Escherichia coli	organophosphates
Flavobacterium	hydrocarbons, pentachlorophenol
Fusarium solani	propanil
Geotrichum marinum thirumalachar	petroleum
Helminthosporium	carbofuran
Hydrogenomonas	halogenated hydrocarbons
Hyphomicrobium	sodium methyl sulfate, etc.
Klebsiella	PCB, toluene
Micrococcus	branched hydrocarbons, hydrocarbons
Moraxella	benzene
Mycobacteria	aromatics, branched hydrocarbons, cycloparaffins
rhodochrous	benzene
Nocardia	hydrocarbons, monoalkylbenzenes, naphthalene, phenoxyacetates, polycyclic aromatics
Propionibacterium pentocaceum	organophosphates
Pseudomonas	4-alkyltoluenes, alkyammonium, alkylamine oxides, anthracene, benzene, heavy metals, hydrocarbons, malathion, methylnaphthalenes, naphthalene, organophosphates, p-cumene, p-xylene, parathion, PCB, pentachlorophenol, phenanthrene, phenoxyacetates, phenylureas, polycyclic aromatics, rubber, secondary alkylbenzenes; (continued)

TABLE 3 (Cont'd)

EXAMPLES OF POLLUTANT-DEGRADING MICROORGANISMS AND SUBSTRATES[a]

MICROORGANISM	POLLUTANT(S)
aeruginosa	oleaginous materials, pulp by-products
cepacia	halogenated hydrocarbons, 2,4,5-T
cepacia var. niagarous	halogenated hydrocarbons
fluorescens	chromates, surfactants
paucimobilis	cyanides, thiocyanates
putida	phenolics, toluene
strutzeri	orcinol
Rhizoctonia solani	alachlor, phenylurea
Rhizopus	PCB
Scolecobasidium	petroleum hydrocarbons
Serratia marascens	bis (2-ethylhexyl) phthalate
Strain DCBI (Tiedge)	chlorobenzoate
Streptococcus faecalis	organophosphates
Streptomyces	diazinon, halogenated hydrocarbons, phenoxyacetates
Thiobacillus ferroxidans	sulfur
Trichosporon	pulp mill lignins, various phenols
Xanthomonas	hydrocarbons, polycyclic aromatics, pulp mill lignins, various phenols
Zylerion xylestrix	cyclodiene type pesticides/ herbicides

[a] Sources: McCormick, 1985; Ouellette and Cheremisinoff, 1985.

TABLE 4

BIODEGRADATION ENHANCED BY THE INTERACTION OF MICROBES[a]

ORGANISMS	COMMENTS
Hydrogenomonas sp. and *Arthrobacter* sp.	A. grew on p-chlorophenylacetic acid produced from DDT[b] by H.
Pseudomonas sp. and *Achromobacter* sp.	The pair grew on Silvex[c], but not the individual strains. Chloride, CO_2 and a small amount of 2,4,5-trichlorophenol was produced.
Bacillus polymyxa and *Proteus vulgaris*	P. produced nicotinic acid required by B.; B. produced biotin required by P.
Chlorobium limicola and *Desulfovibrio* sp.	C. used HS^- as electron donor producing SO_4^{2-}; D. used SO_4^{2-} as electron acceptor, producing HS^-.
Saccharomyces cerevisiae and *Lactobacillus casei*	S. produced riboflavin required by L.
Nitrosomonas sp., *Nocardia altantica* and *Pseudomonas* sp.	The conversion of NH_4^+ to NO_2^- by Nit. increased in the presence of Noc. and P.
Lactobacillus plantarum and *Streptococcus faecalis*	L. produced folic acid required by S.; S. produced phenylalanine required by L.
Pseudomonas sp., unidentified bacterium, *Trichoderma viride*, *Ps. putida*, budding yeast, *Flavobacterium* sp. and unidentified *pseudomonad*	The first four organisms were primary degraders of Dalapon[d]. The others grew on the waste products of the first four.

TABLE 4 (Cont'd)

BIODEGRADATION ENHANCED BY THE INTERACTION OF MICROBES[a]

ORGANISMS	COMMENTS
Methanobacterium sp. and "S" organism	"S" fermented ethanol to H_2; M. used H_2 for growth and methane formation.
Methanobacterium sp. and *Desulfovibrio desulfuricans*	D. released acetate which was fermented by M. to produce methane.
Pseudomonas putida and *Pseudomonas* sp.	The mixed culture used polyvinyl alcohol as sole carbon source, the isolated strains could not. Ps. sp. degraded PVA but required growth factors from P. put.; P. put. grew on PVA metabolites from Ps. sp.
Three pseudomonads and *Hyphomicrobium* sp.	The pseudomonads oxidized methane; H. used the methanol, preventing its accumulation to levels that inhibit the pseudomonads.

[a] Data complied by Johnston and Robinson, 1984
[b] DDT = 1,1,1-Trichloro-2,2-bis[*p*-chlorophenyl]ethane
[c] Silvex = 2-[2,4,5-Trichlorophenoxy]propionic acid
[d] Dalapon = 2,2-Dichloropropionic acid

TABLE 5

CHARACTERISTICS OF AN IDEAL COMMERCIAL SEED CULTURE

1. Increased expression/activity of degradative pathways.
2. Increased substrate utilization range.
3. Ability of seeded microorganisms to successfully compete/establish themselves in the intended ecosystem.
4. Tolerance of toxicants in the intended ecosystem.
5. Ease of handling and application.
6. Shelf life stability.
7. Non-pathogenic/free of risks.
8. Cost-effective (low dose size and low application frequency).
9. Readily available from supplier.

C5

Evaluation of Phase Partitioning Kinetics at Waste Land Treatment Sites

by D.E. Hockley and W.J. Snodgrass

ABSTRACT

This research is examining phase partitioning kinetics of organic compounds among soil water, soil gas, oily sludge and soil solids phases. These compounds are introduced into soil systems by the application of oily sludges at land treatment sites of petroleum refineries. C-14 tracer techniques are being used to evaluate phenol, toluene, and 2-methyl naphthalene interphase transfer using both batch and column techniques. Flow-interruption techniques have merit for soil columns compared to continuous injection. This paper is limited to defining techniques and giving representative results, as work is ongoing. The results of this work are being used to assess the local equilibrium assumption of conventional assessment models.

1. Introduction

Our present understanding of the persistence and migration of toxic organics in industrial waste land treatment systems is limited by several deficiencies. One major deficiency is our understanding of the rate of release of toxic organics from the relatively immobile soil and waste phases to the highly mobile water and air phases of the unsaturated zone.

In land treatment systems, many nonsteady-state processes occur. Intermittent application of waste, periodic rainfall, adsorption, desorption, volatilization, and the release of toxic contaminants from the applied waste are examples of nonsteady-state processes. In the past, the behaviour of operating sites has been analysed using mathematical models which employ steady-state or time-invariant approximations for many of these processes (e.g., EPA's RITZ land treatment model). Nonsteady-state processes may be important for evaluating decommissioning and clean-up of abandoned sites. The validity of these approximations is the subject of this research.

The broad objective of this study is to define and evaluate nonsteady-state effects in industrial waste land treatment systems with particular reference to the mobility of toxic organics in decommissioned sites. The research includes:

1) a determination of the kinetics of adsorption, desorption, volatilization, and waste solvent - water partitioning for three toxic organics applied in the form of oily wastes to two operating land treatment sites; and

2) a formulation of a mathematical model of four-phase (soil, water, air, waste) partitioning which includes kinetic effects, and its comparison to the local equilibrium assumption. Future work will need to include an evaluation of soil column results under conditions of intermittent infiltration and nonsteady-state waste application.

The work reported in this paper is ongoing at the time of writing. Accordingly, this paper is limited to defining the techniques being used and to giving related results.

2. Literature Review and Conceptual Model

Previous research into the fate of toxic organics in soil systems has primarily focused on pesticides (references 1-4). Much of this research has attempted to include sorption kinetics and other non-equilibrium effects (2). Some studies have included the air phase and the possibility of volatilization (3). Very recent research has examined the effect of discontinuous infiltration and found that greater leaching was observed under steady-state flow conditions than under non-steady conditions. The authors hypothesized that the herbicides tested were allowed to migrate to more stable adsorption sites during the no-flow intervals (4). These recent findings support earlier theories that soil-water partitioning may be a two-stage process which cannot be properly modelled without considering kinetic effects (2).

The behaviour of industrial and municipal contaminants in groundwater has been an active field of research by hydrogeologists (5). Some of this research has demonstrated kinetic effects (6). Unfortunately, the absence of an air phase and the resulting physico-chemical differences mean that many of the phase-partitioning findings from groundwater studies need to be re-examined to determine their applicability to surface soil problems.

Phase partitioning is also an important topic in other fields of environmental research. The correlation of partitioning parameters with other chemical properties has been examined (7). The sensitivity of water quality models to partitioning parameters has prompted interest in models which include kinetic effects and two-stage adsorption in bed sediments (8). A refreshingly different approach to phase partitioning has been the fugacity methods currently receiving much attention (9).

Research into the land treatment of toxic wastes is complicated by the presence of a fourth phase, the solvent in which the wastes are applied to the site. Recent work has focused on the treatability of wastes under different soil and operating conditions and the development of comprehensive models (10-12). These models deal only with time-averaged, steady-state behaviour of operating sites and they presently rely on assumptions of instantaneous phase partitioning equilibrium.

A conceptual model of the four phases is given in Figure 1. The contaminant of concern is initially applied to the land system in a relatively immobile, oily sludge form. Subsequent redistribution transfers the contaminant into water, air and soil phases. The contaminant is transported out of the plow zone by gaseous diffusional processes and by infiltrating rain water. Due to intimate contact between soil water and all other phases, land treatment systems commonly consider interchange between the following phases:

i) waste - water (K_w);
ii) air - water (K_a); and
iii) soil - water (K_d).

The coefficients indicated in Figure 1 are the equilibrium description of interphase relationships. Waste-air and soil-air interchange appear to be negligible except in extremely dry conditions. Movement of contaminants in aqueous phases is assumed to occur only with advection dispersion processes associated with water transport due to the relative immobility of the waste.

3. Batch Methods for Determining Phase Partitioning Coefficients

A set of batch procedures for determining equilibrium and kinetic phase partitioning coefficients were developed and tested. The methods use carbon-14 tracers to allow accurate and inexpensive measurement of concentrations. A typical procedure involves adding carbon-14 labelled compound to a reactor containing two of the phases. The reactor is tumbled to allow equilibration and then centrifuged to separate the phases. Both phases are then analysed to determine the concentration in each over time.

Phase partitioning data obtained from batch tests violates some of the underlying assumptions of ordinary linear and non-linear least squares. Previous work has demonstrated that the application of ordinary regression methods to such data can produce very poor estimates of equilibrium parameters. A method known as error-in-variables method or EVM was used to analyse our data. The results are shown as black lines in Figure 2 (13) for toluene in sludge and soil from a refinery waste land treatment facility near Nanticoke, Ontario. They are maximum likelihood estimates of the equilibrium phase partitioning coefficients. The EVM approach can also be used for non-linear isotherm models. It reduces to simpler regressions when they are appropriate. Criteria for choosing the best regression method can be obtained by starting with an EVM formulation.

Kinetic effects were evaluated in a batch system for all of the interphase transfers indicated in Figure 1. Primary emphasis was placed upon: air-water, soil-water, and sludge-water. Results from the equilibrium measurements were used to estimate rate coefficients and then a mathematical model of interphase kinetics for batch systems used to establish the most appropriate experimental conditions (e.g., solids:solution ratio). A rigorous quality control program allowed evaluation of the various uncertainties of the measurements.

The results of these batch, laboratory scale experiments, indicated that air-water transfer is at equilibrium for three compounds (phenol, toluene, 2-methyl naphathlene) within 1-2 hours. Scale-up to field scale considering the large difference in surface area suggests that equilibrium is attained within a few minutes. Evaluation of sludge-water kinetics was made by injecting the three C-14 labelled compounds into the sludge phase. The kinetics (Figure 3) were relatively noisy due to the small amounts of sludge (0.1 to 10 g) typically used. The small amounts are required experimentally due to their relatively large partitioning into the oil/sludge phase. The data suggests that equilibrium was obtained within an hour for the 3 organic compounds tested in these mixtures.

4. Column Methods for Determining Phase Partitioning Coefficients

Column breakthrough curves allow better estimates of water-solid partitioning kinetics than do batch techniques. A tritium pulse is first used to evaluate residence time/dispersion mechanisms and then C-14 tracer applied to evaluate partitioning kinetics. Both continuous injection and flow-interruption techniques (Figure 4) have been used experimentally.

These conventional techniques can be used for weakly sorbing substances. But strongly sorbing substances (eg., 2-methyl naphthalene) have extremely long residence times of the order of a month or more, especially in high organic matter clay soil. A co-solvent approach (14, 15) was used to increase migration times by increasing the tendency for the chemical to partition into the fluid phase. Results, given in Figure 5, demonstrate that co-solvent data can be extrapolated to aqueous systems.

5. Application of Results

The application of these results of this study is directed, at present, to evaluating the limitation of models which assume equilbrium partitioning.

A very practical problem which can limit the applicability of these models is the spatial variability of soil systems and hence of the phase partitioning coefficients. Soil and waste samples from ten locations at the Nanticoke treatment site have been analysed to deetermine the spatial variability of model parameters. Preliminary calculations show that the effect of phase partitioning can affect predicted infiltration by 100%.

The local equilibrium assumption (LEA) can be assessed by examining combinations of transport velocity and the rate at which partitioning equilibrium is attained. One form of the results is given in Figure 6. It shows the region of LEA applicability for modelling steady-state saturated flow. For example, this chart can be used to relate sorption kinetics onto soil to rates of water movement. Simultaneous inter-relationships of all four phases can be evaluated using a transport model.

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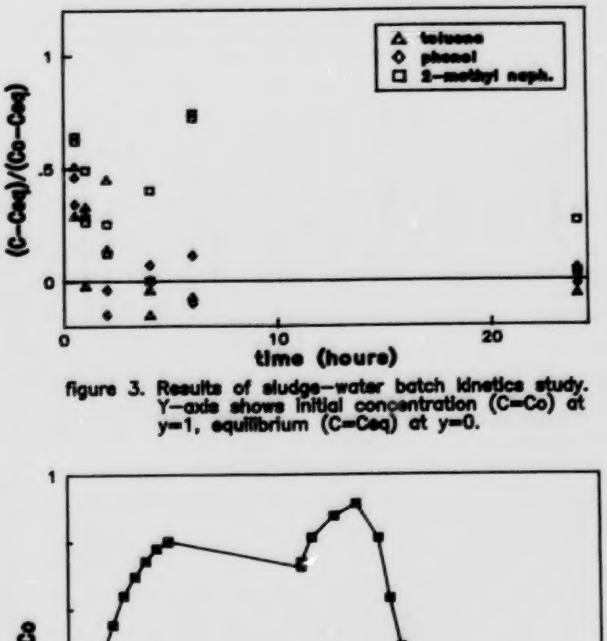

figure 3. Results of sludge−water batch kinetics study. Y−axis shows initial concentration (C=Co) at y=1, equilibrium (C=Ceq) at y=0.

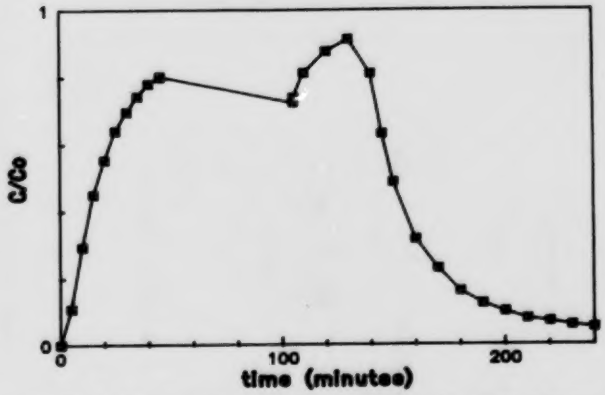

figure 4. Example of flow−interruption btc. Flow stopped from 45 minutes to 105 minutes. Decrease in effluent concentration after interruption is evidence of non−equilibrium effect.

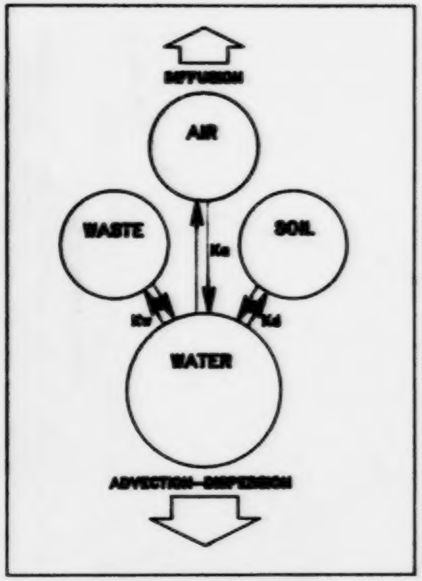
DIFFUSION
AIR
WASTE
SOIL
Ka
Kw
Kd
WATER
ADVECTION–DISPERSION

figure 1. Phase partitioning and transport in land treatment systems.

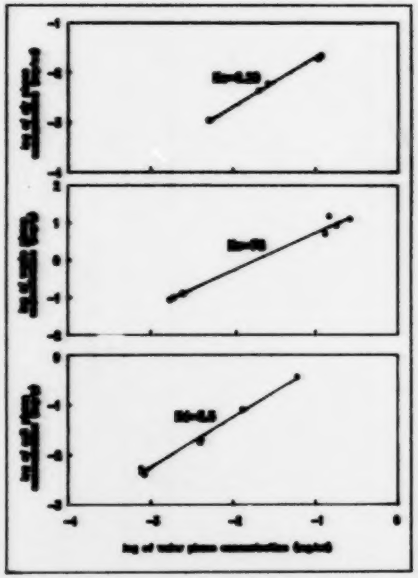

figure 2. Phase partitioning isotherms for toluene (batch results).

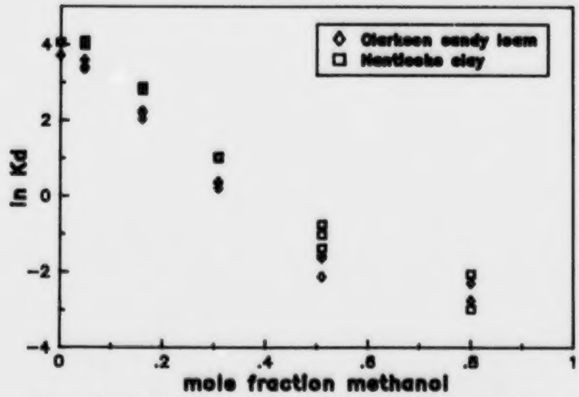

figure 5. Effect of cosolvent on soil–water equilibrium coefficients. Note that log–linear relationship allows extrapolation to aqueous conditions.

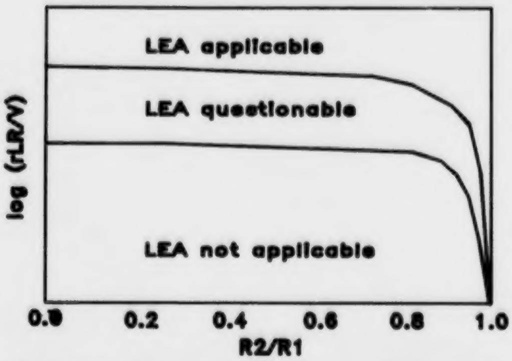

figure 6. Region of LEA applicability for modelling sorption in steady, saturated flow. Y–axis shows ratio of reaction rate (r) to transport time scale (V/RL). X–axis shows ratio of retardation factors with (R1) and without (R2) the kinetically controlled phase.

C6

Preliminary Assessment of a Microfiltration / Reverse Osmosis Process for the Treatment of Landfill Leachate

by

Thomas A. Krug and Sandra McDougall
ZENON Environmental Inc., Burlington, Ontario, Canada

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Abstract

Landfill leachate may contain a variety of toxic inorganic and organic contaminants that are difficult to treat by conventional processes. A potential two stage precipitation/microfiltration (MF) and reverse osmose (RO) process has been evaluated for its suitability in the treatment of landfill leachate. Experiments demonstrated that the precipitation/microfiltration process can be used to remove suspended solids, metals and hardness from raw leachate water generating a product stream suitable for further treatment by reverse osmosis. Membrane flux varied greatly with the precipitation methods used but a stable flux of 170 liters/m^2/hour (LMH) was obtained at recoveries of up to 80%. Reverse osmosis experiments demonstrated the capability of RO in removing residual organics and dissolved solids. Total organic carbon (TOC) and conductivity of 500 mg/l and 7.6 micromhos in the feed to the RO were reduced to 30 mg/l and 0.2 micromhos in the RO permeate. Stable flux rates in excess of 27-30 LMH were obtained at recoveries up to 50% with leachate treated by microfiltration. The processes evaluated can also be useful in the treatment of a variety of complex industrial waste streams.

1.0 Introduction and Background

In recent years, the occurrence of a wide variety of organic and inorganic contaminants in ground and surface water has become recognized as a significant environmental concern by regulatory agencies. Toxic and hazardous compounds can originate from landfill leachates as a result of the soluble components of solid and liquid wastes being leached into surface and groundwater.

Often these landfill leachates are comparable to complex industrial waste streams which contain both toxic organic and inorganic contaminants. In cases where drinking water supplies may be impacted or where there is surface breakout, remedial actions must be undertaken. At some landfill sites leachate which is collected is discharged to municipal sewers for treatment in conventional sewage treatment processes. At other landfill sites where sewer lines are not available the leachate water may be hauled off site for treatment, may be recycled back to the landfill site or may be discharged to a surface water source. Hauling leachate for treatment by conventional processes is expensive and new regulations may limit the discharge of such complex wastes to municipal sewers since the nature of the contaminants are often not appropriate for treatment in conventional municipal biological processes. Recycling leachate within the landfill site itself can reduce the amount of liquid leaving the site but can only provide a short term solution. Effective and inexpensive methods of treating the material need to be developed.

Cross flow filtration processes including microfiltration (MF), ultrafiltration (UF) and reverse osmosis (RO) have been applied to the treatment of a wide variety of industrial waste water streams. Microfiltration processes with a filtration size of 0.1 to 1.0 microns remove suspended solids which are not easily settled and have been applied to the treatment of many wastewaters. In particular they have been successfully employed in the treatment of metal contaminated wastewater as the solids removal step after chemical precipitation of toxic metals. The MF process provides assured discharge water quality and is less susceptible to upset conditions than conventional solids removal processes.

Ultrafiltration processes which operate in a smaller filtration range (0.002 - 0.1 microns) are commonly used for the concentration of wastewater containing emulsified oils or large molecular weight organic contaminants.

Reverse Osmosis processes with a filtration range of less than 0.002 microns are used for the removal of dissolved solids and organic contaminants. Considerable work has been done evaluating the use of RO for the removal of problematic compounds in a variety of waste streams. Some of these include wastewater from electroplating, petroleum, petrochemical, pulp and paper and food processing plants. Researchers have also investigated the possibility of using reverse osmosis for the treatment of landfill leachates.

Chian and DeWalle (1976) of the University of Illinois studied leachate characteristics and related these findings to the most effective treatment method to utilize. Data analysis of the ratios of parameters such as BOD/COD and COD/TOC revealed that the leachate from young landfills containing mainly free volatile fatty acids can be degraded by biological means whereas old fills containing refractory organics were more effectively treated using physical/chemical methods. They also concluded that of all the physical/chemical methods evaluated reverse osmosis membrane treatment was the most effective in removal of COD from leachate water. They also concluded that appropriate pretreatment of leachate prior to reverse osmosis processing would be necessary to prevent severe membrane fouling.

Slater of Manhattan College and Ahlert and Uchrin of Rutgers University (1983) investigated different treatment trains in conjunction with RO to treat landfill leachates. Pretreatment consisted of the removal of bulk oil using gravity seperation, coagulation using lime, recarbonation, then pH adjustment with sulfuric acid. After each chemical addition, the precipitate was allowed to settle before the supernatant was sent to the next treatment stage. The feed to the RO contained 16,400 mg/l of TDS, 26,400 mg/l of COD, and 8,480 mg/l of TOC. The product water from the pretreatment train still contained the majority of the organic matter and the inorganic salts. RO treatment effectively removed 98% of the TDS, 68% of the COD, and 59% of the TOC. The permeate flux averaged 7.5 LMH. Another pretreatment train investigated by these researchers (Slater et.al. 1986) involved lime coagulation, recarbonation, sedimentation, biological treatment and filtration prior to RO. The RO unit was operated in concentration mode. The initial feed TDS and TOC were 13,180 mg/l and 110 mg/l respectively. Treatment by RO was found to be effective with an average TDS removal of over 99%. TOC rejection increased during the testing from 70.8% to 94.7%. The permeate flux averaged 12 LMH at a recovery level (percent of feed flow discharged as clean water) of 63%.

In Canada, Environment Canada is the only public agency which has recently investigated RO for related applications. Over the last few years, a mobile self-contained RO unit has been used by researchers at the Environmental Protection Service (EPS) to demonstrate RO technology. Testing of this RO units at a municipal landfill site containing hazardous wastes from government laboratories demonstrated that RO was an efficient method for concentrating dilute organic leachates (Whittaker et.al., 1985). High removals of organic contaminants such as 1,1-dichloroethane (85.3%), 1,2 dichloroethane (85.5%), diethyl ether (77.2%), 1,4-dioxin (86.6%) were achieved at recovery levels in excess of 90%.

This current project involves the assessment of a two stage process for the treatment of landfill leachates involving precipitation and microfiltration for removal of toxic metals and suspended solids and concentration of residual organics by reverse osmosis. The first step precipitation/microfiltration provides a simple pretreatment process prior to RO. The solids generated in this first stage of the process can be dewatered in a plate and frame or similar filter press and solidified prior to final disposal. The treated water is free of suspended solids which if present would cause problems in the operation of the RO system.

The RO process concentrates the residual organics and dissolved solids and generates a treated water stream with only very low levels of organic contaminants. The concentrated organics may be recycled back to the landfill site where natural biological activity will degrade much of the organic fraction. The biological activity will be enhanced as a result of the reduced level of metals which can inhibit biological degradation. The clean water discharged will balance the water input via rainwater to allow for long term recycle of leachate without excessive build up of water at the site. A process flow schematic for the proposed process is shown in Figure 1.1.

This work has been conducted to evaluate the efficiency and determine operating parameters for each of the steps in the process.

2.0 Experimental Program

2.1 Microfiltration Experiments

Microfiltration experiments were conducted using samples of leachate collected from a landfill site in Southern Ontario. The test equipment consisted of a membrane test unit for 13 mm diameter tubular membranes, a 50 liter process tank, a recirculation pump, interconnecting piping and controls for maintaining the desired operating temperature, pressure and flows. The microfiltration membranes used were manufactured by ZENON Environmental Inc. The equipment could be operated with the permeate recycled to the process tank (stability mode) or collected in a separate tank (concentration mode). A sketch of the equipment used for these tests is shown in Figure 2.1. The membrane test unit allows for testing of six individual 300 mm long sections of 13 mm diameter tubular membranes. The membranes used were ZENON microfiltration membranes. The fluid flow in the tubes is the same as that used in full scale tubular membrane modules and scale up from the small test unit is easily done. The flow though the 13 mm diameter tubes was maintained at 12 liters/min. and the inlet pressure was maintained between 207 - 241 kPa (30 - 35 psig).

Four different chemical precipitation treatment methods were used to precipitate the metals and other contaminants, from the raw leachate water in the five tests conducted. In the first one, caustic soda (sodium hydroxide) was added to the raw leachate to a pH of 10. In the second and fourth test the pH of the leachate was adjusted to 10 by the addition of lime. In the third test, the pH was adjusted to 10 with lime, and 20 g/L of powdered activated carbon (PAC) was also added. In the fifth and final test the pH was adjusted to 10 with lime. Soda ash (sodium carbonate) was also added in this final test to assist in the removal of calcium and magnesium.

In the first three experiments, the microfiltration process was operated in a stability mode with all the treated water or permeate recycled back to the process tank. In the final two experiments, the permeate was collected and the suspended solids in the feed were concentrated by a factor of 10. This concentration represents a 90% recovery since 90% of the volume in the feed was recovered as clean or treated water.

Chemical analyses were conducted on the raw leachate samples, and permeates generated. Flux or permeate rates were measured and recorded at regular intervals during each of the tests. The efficiency of the process in removaling metals and organic contaminants was evaluated.

2.2 Reverse Osmosis Experiments

Reverse osmosis (RO) experiments were conducted using a sample of leachate water which had been processed by the precipitation/microfiltration pretreatment. In the pretreatment the pH of the raw leachate was adjusted to 10 with the addition of lime slurry. Soda ash was also added to assist in the removal of calcium. The resulting solution was then processed in the tubular microfiltration until 90% of the original volume of feed was collected as pretreated permeate. The pH of the MF permeate was adjusted to 5.5 by addition of HC1 to reduce the potential for scale formation during reverse osmosis concentration. In this experiment the MF permeate was also spiked with pentachlorophenol to assess the removal efficiency of this problematic contaminant.

The test equipment consisted of two spiral RO membranes connected in parallel, a 190 liter process tank, a high pressure recirculation pump, interconnecting piping and controls for maintaining the desired operating temperature, pressure and flows. As with the MF experiments the permeate could be recycled to the process tank (stability mode) or collected in a separate tank (concentration mode). A sketch of the equipment used for these tests is shown in Figure 2.2. The spiral RO membranes used were obtained from Filmtec (BW30-2514) and Nitto-Denko (NTR-729HF-52B).

A stability test and two batch concentration experiments were conducted to determine the flux rates and separations which could be obtained with the two different reverse osmosis membranes. The operating pressure of the membranes was maintained at 2,750 kPa and the temperature was maintained at 25°C. Samples of feed and permeate were collected and analyzed to determine the separation of contaminants in the RO process.

3.0 Results and Discussion

3.1 Microfiltration Experiments

The microfiltration flux obtained with the ZENON MF membranes during the first three short duration MF experiments are shown in Figure 3.1. As can be seen from the graph the flux obtained varied greatly depending upon the precipitation chemicals used. When lime was used to adjust the pH of the raw leachate, the MF membranes exhibited a high flux of approximately 254 LMH. When lime and powdered activated carbon were used together the flux was stable at approximately 170 LMH. When the pH was adjusted using caustic the flux was very low at less than 42 LMH. It is apparent that the method of chemical precipitation has a great impact on the flux which is obtained in the microfiltration process. The solids formed when caustic is used appear to have a greater tendency to adhere to and foul the MF membranes. The flux obtained with lime and lime plus activated carbon are slightly lower than is normally obtained with the MF membranes in standard metal precipitation processes but no abnormal levels of fouling appear to be occurring.

The microfiltration flux obtained during the final two longer duration MF experiments with lime and lime plus soda ash are shown in Figure 3.2. This graph shows the flux during concentration of the feed to one tenth its original volume (90% recovery). The flux for test #4 when lime alone was used was stable at 170 LMH during most of the concentration cycle. The flux did however decline rapidly after the 80% volume reduction point. This loss in flux at high concentration may be the result of fouling of the membrane which occurs when a high concentration of some slurry component is present. The flux for test #5 when lime and soda ash were both used as precipitation chemicals was stable near 85 LMH for the latter half of the concentration run. The flux was lower than the previous test but did not decline during the final concentration to 90% volume recovery. As in the first set of MF experiments, the flux is highly dependent upon the precipitation chemicals used.

The performance of microfiltration membranes are affected by the chemicals used and by the specific chemistry of the membrane polymer and membrane additives used. Certain additives can repel particular compounds which may be causing fouling of the membrane and allow for much higher and more stable flux rates to be obtained. The results obtained here are for one type of microfiltration membrane chemistry and optimization of the particular membrane chemistry may yield higher and more stable flux for this particular application. Optimization of the dosage of the precipitation chemicals will also likely result in improved membrane performance.

The results of chemical analysis on raw leachate and microfiltration permeate from the first three MF experiments are shown in Table 3.1. As expected total suspended solids (TSS) were virtually completely removed by the microfiltration process with all of the cheimcal precipitation method while total dissolved soilds (TDS) shows almost no reduction. Total Organic Carbon (TOC) levels were reduced slightly (10 - 11%) with use of caustic and lime and somewhat more (32%) with the combined lime plus carbon treatment. Total organic halogens (TOX) were reduced to a considerably higher degree than the rest of the organic carbon particuarly when activated carbon was used in addition to the lime. Calcium was removed almost completely when casutic (NaOH) was used to adjust the pH but very little when lime (Ca $(OH)_2$) which contains additional calcium was used. Few metals were present in the raw leachate sample but iron was present at 130 mg/l. Iron was completely removed by microfiltration after treatment by all three precipitation methods used. Xylene and toluene were present in the raw feed and appear to have been completely removed in the microfiltration process. This reduction may be due to the organics being associated with solids which are rejected or may be the results of loss due to volatilization. Longer term testing with large sample volumes will be required to determine the actual rejection of these organics.

The results of chemical anlaysis on raw leachates and MF permeate from the fourth and fifth MF experiments are shown in Table 3.2. As was seen in earlier experiments, suspended solids are removed but dissolved solids pass through the microfiltration membrane. Organic carbon was reduced only slightly and organic halogens as measured by TOX were not reduced at all. The major difference in the MF permeate after pretreatment with lime and lime plus soda ash are in the levels of calcium and alkalinity which are both significantly less when soda ash was used. The addition of soda ash has had the desired effect of softening the water to make it more suitable treatment in the RO polishing process.

3.2 Reverse Osmosis Experiments

The flux for the Filmtec and Nitto membranes during the two batch concentration experiments are shown in Figure 3.3. The flux for the Filmtec membrane remained virtually the same for both the concentration tests at 27 - 30 LMH. There was a slight decrease in the flux during the concentration but this flux loss was recovered when fresh dilute feed was processed in the subsequent batch. This suggests that the flux loss was due to changes in the material being processed during concentration rather than serious fouling of the membrane. The flux for the Nitto membrane at the end of the first concentration run was 30 LMH but increased significantly during the second batch concentration to 47 LMH.

The recovery during the test was limited to 50% since in this application the concentrate may be easily disposed of by recycle back to the landfill site. The flux was still stable at this 50% recovery level and in other wastewater applications where disposal of concentrate is more difficult it may be possible to increase the recovery level without significant loss in flux.

During each of the batch concentration runs, samples of permeate were collected and the conductivity was measured. Table 3.3 shows the conductivity of the feed and permeate collected during the two batch concentration runs. The rejection of conductivity for the Filmtec membrane was consistently 99% or better. The rejection of conductivity for the Nitto membrane was considerably lower and decreased significantly at the end of the 2nd concentration run. This loss in conductivity rejection and increase in flux may be due to some deterioration in the membrane as a result of exposure to the leachate solution or may be the result of a small leak around some mechanical seal in the membrane module itself.

As a result of the consistent flux and high conductivity rejection, more detailed chemical analysis was conducted on the permeate from the Filmtec membrane generated during the final batch concentration test. Results of this analysis are shown in Table 3.4. Measurements of organic content including TOC, BOD and TOX showed virtual complete rejection (98%) or organic compounds. All inorganic compounds which were present above the minimum detection limit with the exception of boron showed rejection of at least 97%. Very few heavy metals were present in the original feed and those that were present were removed in the precipitation microfiltration pretreatment. The RO rejected virtually all (98%) of the dissolved solids as measured by conductivity from the RO feed.

The feed to the RO system had been spiked with pentachlorophenol (PCP) and toluene. The feed to the RO contained 430 ppb of PCP and 320 ppb of toluene. The permeate contained 30 ppb of PCP and 100 ppb of toluene demonstrating 93% rejection of PCP and 69% rejection of toluene.

The reverse osmosis experiments demonstrated the feasibility of RO for the concentration of residual organics and dissolved solids present in the permeate from a microfiltration process. The flux for the Filmtec membrane was stable through the duration of the testing. Rejection of organics as measured by general parameter of TOC, BOD and TOX was excellent. Rejection of volatile organics such as toluene were significant but somewhat lower.

4.0 Conclusions

The results of this work has demonstrated the feasibility of a two step process for the treatment of landfill leachate containing a complex mixture of inorganic and organic contaminants. The first stage precipitation/microfiltration step was capable of removing suspended solids, metals and hardness from the raw leachate. These contaminants will interfer with the operation of RO systems downstream in the process and can reduce the rate of biodegradation of organics in the leachate if biological treatment is used. The process is resistant to upset and provides a consistent high quality product water required for RO processing. The RO process has been shown to be capable of concentrating virtually all the remaining organics and dissolved solids present from the first stage of treatment and generating a clean product water with very low levels of any problematic contaminants. The process of precipitation/microfiltration can be used for removal of suspended solids, metals and other contaminants in a variety of wastewater applications. With suitable pretreatment, reverse osmosis can be used as an important step in the treatment of many different wastewater streams. Pilot testing of the proposed process needs to be conducted to confirm the efficiency of the process during longer term operation.

Acknowledgement

The authors wish to acknowledge the assistance of Environment Ontario who has provided funding for this work.

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FIGURE 1.1

Microfiltration / Reverse Osmosis Process For Leachate Treatment

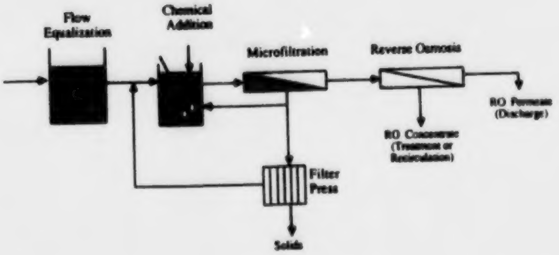
Flow
Equalization
Chemical
Addition
Microfiltration
Reverse Osmosis
RO Permeate
(Discharge)
RO Concentrate
(Treatment or
Recirculation)
Filter
Press
Solids

FIGURE 2.1

Flow Schematic of Microfiltration Test Equipment

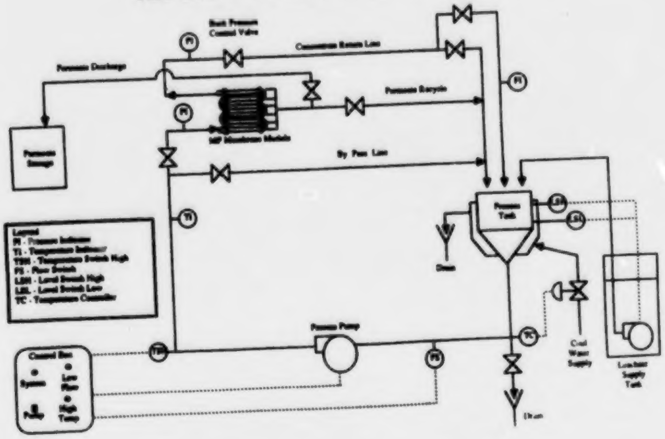
Back Pressure
Control Valve
PI
Concentrate Return Line
Permeate Discharge
PI
Permeate Recycle
PI
MF Membrane Module
Permeate
Storage
By Pass Line
Process
Tank
LSH
LSL
TI
Drain
Legend
PI - Pressure Indicator
TI - Temperature Indicator
TSH - Temperature Switch High
FS - Flow Switch
LSH - Level Switch High
LSL - Level Switch Low
TC - Temperature Controller
Process Pump
TC
Cool
Water
Supply
Leachate
Supply
Tank
Control Box
System
Low
Flow
Pump
High
Temp
TSH
FS
Drain

FIGURE 2.2

Flow Schematic For Reverse Osmosis Test Equipment

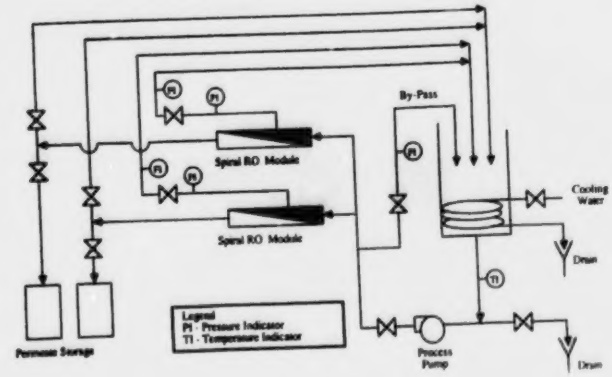
By-Pass
PI
PI
Spiral RO Module
PI
PI
PI
Spiral RO Module
Cooling Water
Drain
TI
Legend
PI - Pressure Indicator
TI - Temperature Indicator
Permeate Storage
Process Pump
Drain

FIGURE 3.1

Flux Rates for Short Duration Microfiltration Experiment

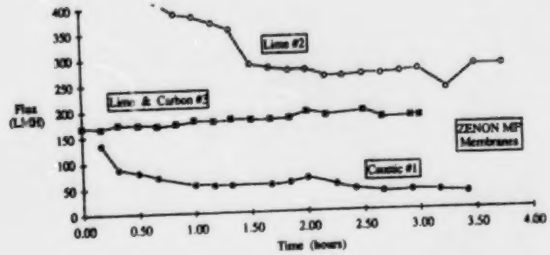

FIGURE 3.2

Flux Rates for Longer Duration Microfiltration Experiments

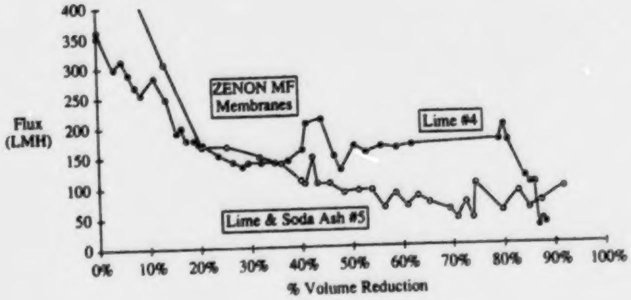

FIGURE 3.3

Flux Rates for Reverse Osmosis Concentration Tests

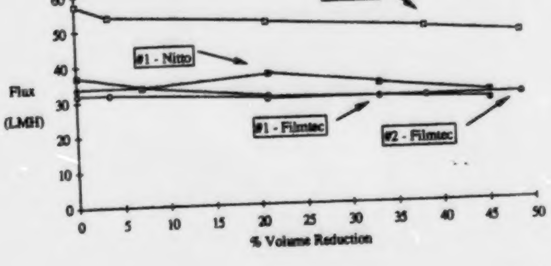

TABLE 3.1

Product Water Quality for Microfiltration Experiments 1, 2 & 3

Parameter	Raw Feed	Test # 1		Test # 2		Test # 3	
		Permeate	% Rejection	Permeate	% Rejection	Permeate	% Rejection
pH	6.8	9.7	--	10	--	9.9	--
TSS (ppm)	290	6.5	98%	2.7	99%	1.5	99%
TDS (ppm)	6930	8530	-23%	5790	16%	4970	28%
TOC (ppm)	1900	1710	10%	1690	11%	1290	32%
TOX (ppb)	228	110	52%	31.4	86%	4.3	98%
Calcium (ppm)	570	5.7	99%	510	11%	450	21%
Magnesium (ppm)	380	200	47%	140	63%	110	71%
Iron (ppm)	130	0.029	>99%	<0.01	>99%	<0.01	>99%
Xylene (ppm)	0.11	<0.02	>82%	<0.02	>82%	<0.02	>82%
Toluene (ppm)	0.14	0.04	71%	0.02	86%	<0.01	>93%

Chemical Pretreatment:
Test # 1 - Caustic to pH10.
Test # 2 - Lime to pH 10.
Test # 3 - Lime to pH 10 and 20 g/l Powdered Activated Carbon (PAC).

TABLE 3.2

Product Water Quality for Microfiltration Experiments 4 & 5

Parameter	units	Test 4			Test 5		
		Raw Feed	Permeate	% Rejection	Raw Feed	Permeate	% Rejection
pH		6.6	11.9	–	7.0	10.7	–
TSS	(ppm)	430	21	95%	200	60	70%
Turbidity	(NTU)	3.6	0.47	87%	24	0.6	98%
TDS	(ppm)	6,100	6,680	-10%	–	–	–
Conductivity	(mmhos)	5.07	6.86	-35%	4.14	4.80	-16%
TOC	(ppm)	1,650	1,400	15%	–	–	–
TOX	(ppb)	100	120	-20%	–	–	–
COD	(ppm)	4,700	4,300	9%	–	–	–
BOD	(ppm)	3,500	3,000	14%	–	–	–
Fluoride	(ppm)	interference	interference			130	
Chloride	(ppm)	670	930	-39%		3,600	
Nitrite (as N)	(ppm)	<0.2	<0.2			<0.20	
Bromide	(ppm)	<0.8	<0.8			<0.8	
Nitrate (as N)	(ppm)	0.96	1.0	-4%		1.0	
Phosphate (as P)	(ppm)	<0.8	<0.8			<0.8	
Sulfate	(ppm)	380	390	-3%		<1.0	
Alkalinity (as CaCO3)	(ppm)	2600	2800	-8%		240	
Calcium	(ppm)	540	1100	-104%	400	22	95%
Magnesium	(ppm)	240	1	>99%	340	140	59%
Sodium	(ppm)	430	420	2%	560	2000	-257%
Potassium	(ppm)	240	230	4%	250	260	-4%
Aluminum	(ppm)	1	0.3	70%	0.75	<0.03	>96%
Barium	(ppm)	0.063	0.071	-13%	0.75	0.003	>99%
Boron	(ppm)	5.2	4.1	21%	5	3.6	28%
Chromium	(ppm)	0.15	<0.1	>99%	0.075	0.012	84%
Iron	(ppm)	79	<0.2	>99%	75	0.094	>99%
Manganese	(ppm)	7.1	2.9	59%	4.5	0.007	>99%
Nickel	(ppm)	0.15	<0.1	>33%	<0.05	0.074	
Phosphorus	(ppm)	4.7	2.6	45%	3.7	0.96	74%
Silicon	(ppm)	12	1.1	91%	10	3.3	67%
Strontium	(ppm)	5.3	1.2	77%	5.9	0.18	97%
Titanium	(ppm)	0.91	0.85	7%	<0.05	<0.01	
Zinc	(ppm)	2.4	<0.1	>96%	2	0.019	99%
trans-1,2-Dichloroethene	(ppb)	4.1	<3.0	>27%	<1.0	<1.0	
1,1-Dichloroethane	(ppb)	60	<3.0	>95%	100	7.2	93%
1,2-Dichloroethane	(ppb)	5.9	<3.0	>49%	25	2.7	89%
Benzene	(ppb)	7.1	<3.0	>58%	59	5.7	90%
Toluene	(ppb)	79	36	54%	550	320	42%
Ethyl benzene	(ppb)	4.2	3.3	21%	79	1.5	98%
Tetrachloroethane	(ppb)	8.1	<3.0	>63%	<1.0	<1.0	
Phenol		3.9	1.1	72%			

Other Cations were less than detection limit.

Chemical Pretreatment:
Test # 4 - Lime to pH 10.
Test # 5 - Lime to pH 10 & Soda Ash.

TABLE 3.3

Conductivity of Reverse Osmosis Permeate

Test	Feed	Filmtec		Nitto	
		Permeate	% Rejection	Permeate	% Rejection
Concentration #1	13.8	0.19	99%	1.4	90%
Concentration #2	13.3	0.15	99%	2.17	84%

TABLE 3.4

Product Water Quality from Reverse Osmosis Experiment

Parameter	Unit	Spiked RO Feed	Filmtec Permeate	% Rejection
pH		6.1	5.2	–
TSS	(ppm)	–	–	–
Turbidity	(NTU)	6	0.4	93%
TDS	(ppm)	7500	–	–
Conductivity	(mmhos)	7.61	0.19	98%
TOC	(ppm)	1500	30	98%
TOX	(ppb)	200	2.1	99%
COD	(ppm)	5,900	–	–
BOD	(ppm)	4,900	35	99%
Fluoride	(ppm)	130	3.8	97%
Chloride	(ppm)	3,600	36	99%
Nitrite (as N)	(ppm)	<0.2	<0.2	–
Bromide	(ppm)	<0.8	<0.8	–
Nitrate (as N)	(ppm)	1.0	<0.20	>80%
Phosphate (as P)	(ppm)	<0.8	<0.8	–
Sulfate	(ppm)	<1.0	<1.0	–
Alkalinity (as CaCO3)	(ppm)	240	–	–
Calcium	(ppm)	22	0.076	>99%
Magnesium	(ppm)	140	0.38	>99%
Sodium	(ppm)	2,000	40	98%
Potassium	(ppm)	260	8.2	97%
Aluminum	(ppm)	<0.03	<0.03	–
Barium	(ppm)	0.003	<0.001	>66%
Boron	(ppm)	3.6	0.83	77%
Chromium	(ppm)	0.012	<0.01	>16%
Iron	(ppm)	0.094	<0.01	>89%
Manganese	(ppm)	0.007	<0.005	>28%
Nickel	(ppm)	0.074	<0.01	>86%
Phosphorus	(ppm)	0.96	<0.1	>89%
Silicon	(ppm)	3.3	<0.05	>98%
Strontium	(ppm)	0.18	<0.001	>99%
Titanium	(ppm)	<0.01	<0.01	–
Zinc	(ppm)	0.019	<0.01	>47%
1,1-Dichloroethane	(ppb)	7.2	<1.0	>86%
1,2-Dichloroethane	(ppb)	2.7	<1.0	>63%
Toluene	(ppb)	320	100	69%
Total Phenol	(ppb)	430	30	93%

C7

ANAEROBIC TREATMENT OF LANDFILL LEACHATE

G. P. Vicevic, B. J. Forrestal, A. Stevenson
ORTECH International (Formerly Ontario Research Foundation)
Mississauga, Ontario

ABSTRACT

Leachate generation at landfill sites continues to be a serious environmental problem. It is, therefore, necessary to address this with a suitable treatment scheme. The enhanced sanitary landfill (ESL) was developed at ORTECH (formerly Ontario Research Foundation) to provide leachate treatment and, at the same time, relatively fast land reclamation.

A pilot scale anaerobic digester was constructed and operated over a one-year period at the Region of Peel's Britannia Road Landfill Site in Mississauga to investigate the treatability of landfill leachate. In this paper, the results of the programme are presented and discussed.

INTRODUCTION

The sanitary landfill has been, and continues to be the principal means of municipal solid waste (MSW) disposal in Ontario. Through improved site selection, design and operation, both aesthetic and environmental problems have been reduced considerably. Despite these advances, groundwater contamination by leachate, and toxic and combustible gas generation continue to be problems at many landfill sites. Furthermore, the sanitary landfill is a land intensive process which can have significant economic and social consequences, particularly in growing urban areas. Uncontrolled generation of gas and leachate prevents timely reclamation of the land for subsequent sale or reuse. Although biogas abstraction systems have been installed at many landfills, there are several drawbacks, notably low methane recovery efficiency and limited control of methane generation rates. In recognition of the need for additional pollution control for sanitary landfills, ORTECH has developed the enhanced sanitary landfill.

THE ENHANCED SANITARY LANDFILL

The enhanced sanitary landfill concept is based on the premise that the landfill should be designed not as a dump, but as a waste treatment reactor. This reactor must be designed and operated in such a way as to maximize the biodegradation rate of the MSW. It is believed that this can best be achieved by segregating the biodegradation process: hydrolysis/acidogenesis in the landfill and methanogenesis in a separate vessel. Treated leachate is recycled back to the landfill to continue the process. Saturation of the MSW is necessary to optimize the process, thereby taking advantage of the full landfill active surface area. By promoting methanogenesis in an external vessel, accelerated and more complete volatile-fatty-acid (VFA) conversion, and improved methane yields and production will result. It is estimated from published work that the organic fraction in the active landfill cell can be largely degraded within five years.

PHASE I: PILOT SCALE DEMONSTRATION

In order to further evaluate the concept of the enhanced sanitary landfill, a pilot facility was installed at Peel Region's Britannia Road sanitary landfill site in Mississauga. Phase I of this trial is a demonstration of the anaerobic treatability of leachate, in an external vessel. The treatment facility is illustrated in Figure 1.

The reactor was a 1.7 m^3, upflow, fixed film anaerobic digester, constructed of fibreglass reinforced polyethylene. The packing used was Statiflow's Modular PVC Media, providing over 90 m^2 of surface area per m^3 of volume. The reactor was operated with a 2 L/min recycle rate and at a temperature of ~ 35°C. Biogas was measured by a cumulative liquid displacement flowmeter and vented to atmosphere. Leachate was pumped from a landfill works common sump to a 1 m^3 surface equalization tank. From the equalization tank, it was pumped through a hot water heat exchanger and brought to a temperature of 35°C. Treated leachate was discharged to the sanitary sewer. The leachate was found to have sufficient nitrogen content but was deficient in phosphorus. As a result, supplemental phosphorus was added in the form of dissolved di-ammonium phosphate.

The pilot facility was installed to provide the necessary design information to scale up for Phase II in which the complete ESL concept will be demonstrated. It was believed that a one-year operating duration would provide suitable data for this objective.

The anaerobic digester was seeded with anaerobic supernatant from Mississauga's Clarkson sewage treatment plant in October of 1987. Throughout the remainder of the year and into January of 1988, biogas production and COD reduction were extremely poor. It was felt that this was due, mainly, to an insufficient seeding of anaerobic bacteria. Consequently, in February, the reactor was reseeded with anaerobic sludge from Clarkson. Following this reseeding, digester performance quickly began to improve.

As unit performance continued to improve, the organic loading was increased in an attempt to determine the maximum tolerable leachate throughput. Table 1 is a summary of the digester performance data from June 2 to September 8, 1988.

At the time of writing this paper, the most current data available have the anaerobic digester operating at an organic loading of 2.7 kg COD/m^3 reactor/day, with a hydraulic retention time (HRT) of 2.3 days. COD and BOD removal are in the 80% and 85% range respectively. Biogas production is in the 1000 mL/min range with a methane content of between 70 and 75% (v/v).

The digester has also demonstrated the ability to remove some heavy metals from the leachate at varying removal efficiencies. Zn, B, Fe, Mn, Ca, Mg and Ni have all been removed from the wastewater at efficiencies ranging from 50-95%. It is believed that these metals have been bioaccumulated in the anaerobic sludge, and this has been confirmed by sludge metal scans which show very high levels of these particular metals.

Through the experimental program, the reactor has demonstrated extreme resilience to process upsets. First and foremost, the leachate feed to the digester has been variable. Figure 2 illustrates the heterogenous nature of leachate COD. Despite this, reactor performance did not appear to cycle. Moreover, other process upsets, such as temperature control failure and feed interruption for greater than 60 hours did not have a long-term effect on COD removal or biogas production. Within one or two days, the anaerobic digester was operating at the same efficiency as before the process upset.

This characteristic, along with the relatively high alkalinity of the Britannia leachate (> 3000 mg $CaCO_3$/L) made anaerobic digestion a particularly suitable technology for treating Britannia leachate. The results of the programme indicate that anaerobic treatment of leachate is a feasible and effective form of pollution control. Also, the biogas production rates and high methane concentration further demonstrate the high efficiency of this treatment alternative. In general, the results of this study have confirmed the Phase I objectives and lead to the necessity of a demonstration of the entire enhanced sanitary landfill scheme.

PHASE II: INTEGRATED ENHANCED LANDFILL SYSTEM DEMONSTRATION

With the successful completion of Phase I, ORTECH has proposed that Phase II be undertaken as a demonstration of the entire enhanced sanitary landfill concept. It would encompass construction of the landfill test cells, one enhanced, the other a control. Nominal dimensions would be 10 m x 10 m x 3 m deep. The pumping/recycling network would be installed prior to MSW landfilling. A 25 m^3 anaerobic digester would be constructed alongside the cell, based on the design information provided from Phase I. A comprehensive monitoring program, including stratigraphical, hydrogeological, physical chemical and biochemical analyses would be conducted during the estimated 2-3 year operating time. When leachate quality and gas production are indicative of landfill stabilization, recycling would be terminated and an intensive final assay conducted at the site to assess the final conditions of the landfill.

ACKNOWLEDGEMENTS

This project was funded by the Ontario Ministry of the Environment, Waste Management Branch. The authors wish to acknowledge the support and assistance of the MOE and the Region of Peel's Department of Public Works, Engineering and Abatement Division.

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TABLE 1 - Britannia Leachate Treatment Study:
Digester Performance Data Average - June 2 - September 8, 1988

BOD Removal (%)	COD Removal (%)	Organic Loading (kg COD/m^3 reactor/day)	HRT (days)	Biogas Production (mL/min)	Biogas Methane Content (% v/v)
83	74	1.8	3.7	689	72

FIGURE 1 - Enhanced Sanitary Landfill: Phase 1 Demonstration Facility

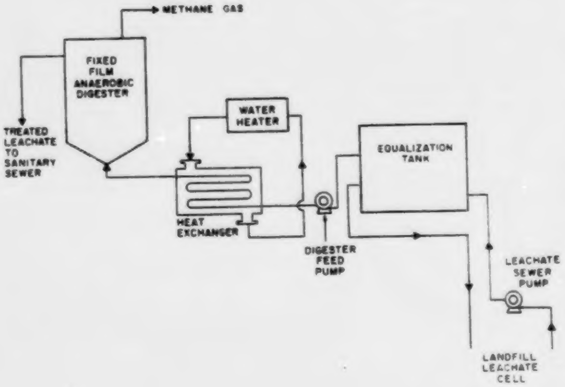
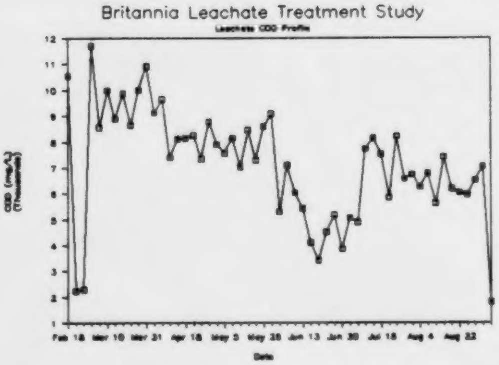

METHANE GAS
FIXED FILM ANAEROBIC DIGESTER
TREATED LEACHATE TO SANITARY SEWER
WATER HEATER
HEAT EXCHANGER
DIGESTER FEED PUMP
EQUALIZATION TANK
LEACHATE SEWER PUMP
LANDFILL LEACHATE CELL

FIGURE 2 - Britannia Leachate Treatment Study



C8

The origin and distribution of methane in the Alliston aquifer complex

R. Aravena, J.F. Barker, M. Bliss,
L.I. Wassenaar and R.W. Gillham

Waterloo Centre for Groundwater Research, University of Waterloo,
Waterloo, Ontario, N2L 3G1.

1. Introduction

Methane gas seems to be a common trace component in groundwater, and a potentially explosive contaminant where present in high concentration. (Hughes et al. 1971; Coleman, 1976; Barker, 1979). This seems to be the case for groundwater in some parts of the Alliston aquifer complex. Many wells that tap this aquifer produce high volumes of methane. As a result, most of the municipal wells have aeration treatment systems. This aquifer is the major water supply for towns such as Alliston, Cookstown and Bond Head, and is an essential water resource for a growing population.

The distribution and origin of methane in this aquifer is not well established. Two hypothesis have been postulated. One suggests that the occurrence of methane is controlled by the nature of the underlying Paleozoic bedrock. Where the bedrock is shaley (Collingwood, Blue Mountain Groups), insignificant amounts of methane are found. However, where the bedrock is limestone (Trenton Group), methane is usually found at high concentrations (T.J. Yakutchik, MOE, pers. comm). This implies that the source of methane is leakage or migration from the more permeable limestone bedrock. This hypothesis is encouraged by the fact that methane is likely present in the Trenton Group. It is well documented that these carbonate rocks are an important reservoir for natural gases in other part of southern Ontario. (Barker and Pollock, 1984).

The second hypothesis, based on carbon isotope analyses of methane from overburden wells, suggests that the methane is of biological origin, produced by bacterial action (Barker, Fritz and Brown, 1979; Barker and Fritz, 1981). Consequently, the methane is being generated within the Alliston sand aquifer, as the methane found in the natural gases in the Trenton rocks has a carbon isotopic composition typical of thermocatalytic methane. Therefore, a bedrock control of the occurrence of methane appears to be unlikely.

This paper presents preliminary results from the first stage of an ongoing research project funded by the M.O.E (1987-89), whose main objective is to produce an unified and acceptable theory about the origin of the methane in the Alliston aquifer complex.

2. Hydrogeology

The Alliston Aquifer complex is a confined, discontinuous, but extensive network of fine to gravelly sand lenses underlain by bedrock or basal till and overlain by clayey till. It seems the aquifer complex extends from the vicinity of Aurora to Wasaga Beach and includes the area northwest along Nottawasaga Bay (Figure 1). This information is based on a map of the aquifer complex published by Turner, MOE (1977) and a recent review of water well records filed at the M.O.E offices.

The study area is mostly underlain by rocks of the Simcoe (middle Ordovician) and Nottawasaga (upper Ordovician) Groups. The areal distribution of the various units that form these groups is shown in Figure 2. The units relevant to this study are the Trenton and Black River limestones and the

Collingwood and Blue Mountain shales. In general, the bedrock is not an important source for water supply, and in some areas the water is highly mineralized and not suitable for domestic or stock purposes.

The overburden material that encloses the aquifer complex is of Pleistocene glacial origin and consists of glacio-lacustrine, glacio-fluvial outwash deposits, and ice-deposited drift (till). The stratigraphy of these deposits is extremely variable vertically and laterally. In general, from the bedrock upward, there occur successions of lacustrine and glacio-lacustrine silts and sands, and/or clays with intercalated lenses, fans, or channels of fluvial or glacio-fluvial sands, and /or gravels interlayered with successions of semi-permeable tills. More detailed information about the overburden materials can be found in Sibul and Choo-Ying (1971). High capacity wells have been developed in many part of the aquifer complex. However, high yielding wells often occur at the margins of the complex. Except for the presence of methane and high iron content in some groundwater, the quality of the water is suitable for water supply.

A simplified piezometric surface map is presented in Figure 3. This map is an updated version of Turner (1977) and includes more wells from the margins of the aquifer system in order to better define regions of recharge, specifically in the area south of the complex. The regional groundwater flow pattern illustrates two major flow systems which are separated by a north-south divide at piezometric elevations greater than 750 feet. One dischargs into Nottawasaga Bay to the north and the other to Kempenfelt Bay and Cooks Bay to the northeast. Recharge is regional from the east and west marginal bedrock highs and possibly from the south in the vicinity of Aurora, where there apparently exists an east-west groundwater flow divide.

3. Approach

3.1 Methane origin and distribution

Methane gas (CH_4) is formed by two distinct processes. One process is the decomposition of organic matter by a group of bacteria called Methanogens. This type of methane is referred to as "biogenic methane". The other process is the thermal degradation of organic material during burial and diagenesis. This type of methane is termed "thermocatalytic methane". These processes are accompanied by carbon and hydrogen isotope effects that characterize the methane with a specific isotopic composition that reflects the processes responsible for the methane formation. Biogenic methane, excluding the methane generated in landfills, are characterized by $\delta^{13}C$ values less than -60 o/oo whereas thermocatalytic methane have values greater than about -45 o/oo (Coleman, 1976; Barker and Fritz, 1981). In addition, the hydrogen isotope (deuterium) concentration of biogenic methanes are related to the deuterium concentration of their associated water. This relationship depends on the type of reactions that are involved in the methane formation (CO_2 reduction vs acetate dissimilation) (Shoell, 1980; Woltemate et al, 1984). This study will use carbon-13 and deuterium isotopes as a tracers to provide information about the genesis of the methane.

The distribution of methane in the Alliston aquifer in not well defined. It seems that the area between Bond Head (Beeton), Alliston, Cookstown, and Aurora contains the major occurrence of methane in the groundwater. However, similar occurrences have been noted in the township of Innisfil, and in bedrock wells near Wasaga Beach. Groundwater from overburden and bedrock wells that represent most of the aquifer will be collected for methane analyses. The methane distribution will be compared with the distribution of the various lithologic units that form the underlying bedrock in order to further test the hypothesis of bedrock control on the presence of methane in the groundwater. Additional gas analyses will include hydrocarbon molecules heavier than the methane. The presence of these type of compounds are an indication of the thermocatalytic origin of methane.

3.2 Carbon sources

The occurrence of methane in any type of environment is intimately linked to its carbon precursor, and/or linked to a source rich in organic matter. Potential carbon sources for the generation of methane in the Alliston aquifer complex are organic matter present in the aquifer material and bedrock and dissolved organic carbon (DOC) in the groundwater. The other alternative is migration of methane from hydrocarbon reservoirs that could exist in Paleozoic bedrock. Information about the nature of these sources, specifically its age or time of deposition could be useful in linking the methane to its carbon precursor. Carbon-14 (^{14}C), a radioactive carbon isotope that is widely used for dating of geological materials, will be used as a dating tool in this study. Radiocarbon analyses will be performed on methane samples, on the two main fractions that form DOC (hydrophobic and hydrophilic), and aquifer kerogen if it is available. In addition, geological information related to the time of deposition of the overburden materials and bedrock units are also available in the literature. The geochemical characterization of the DOC will also provide information about the residence time and the organic geochemistry of the groundwater.

3.3 Origin and residence time of the groundwater

One mechanism postulated for methane migration in aquifers is transport as a dissolved solute in groundwater (Coleman, 1976). Therefore, another important aspect of this study is the origin and the residence time (age) of the groundwater. Radiocarbon analyses of dissolved inorganic carbon (DIC) are a common tool used in hydrological studies to provide information about the residence time of the groundwater. However, in aquifers affected by methanogenesis, this method is very imprecise. Efforts will be made to improve the application of DIC radiocarbon dating in these type of aquifers. Furthermore, the stable oxygen-18 (^{18}O) and deuterium (^{2}H) isotopes that form part of the water molecule will be used as a tracers to provide information about recharge environments, and origin of the overburden and bedrock groundwater.

The geochemical information derived from this study, in combination with existing hydrogeological and geochemical data, is expected to provide a unified theory about the origin and distribution of methane in the Alliston aquifer complex. This research should improve the scientific basis for the prediction of other areas of the Alliston aquifer that may be affected with water quality problems associated with the presence of methane. This approach can also be applied to others aquifers contaminated with methane.

4. Preliminary results and discussion

The first step of this project was to compile existing information regarding occurrence of methane and hydrogeological and geochemical aspects of the Alliston aquifer complex (Bliss, M., 1988).

Field work during summer 1988 has focussed mainly on the collection of groundwater and gas samples stripped from groundwater from deep overburden and bedrock wells for isotopic and chemical analyses. The data presented in this paper corresponds to the southern part of the aquifer complex. The sampling locations can be seen in Figure 4.

4.1 Gas analyses

Chromatographic analyses of gas samples are reported in Table 1. This data shows that the main components of gases extracted from the groundwater are CH_4 and N_2. The average concentration of these two compounds are 80 % and 20% respectively. The samples with high oxygen content indicate air contamination during sampling. No traces of C_2 to C_4 hydrocarbon compounds were found in these samples.

Samples for determination of CH_4 and N_2 concentration were collected in glass syringes and analyzed by gas chromatography. For samples supersaturated with methane (saturation at 25°C is 1310 umol/l), degassing during sampling caused some errors in the determination of gas concentration. All the samples were collected after the pressure tank in domestic wells. Samples with CH_4 levels > 1400 umol/l should be considered with caution. This data is plotted in Figure 4.

It appears that the area southeast of Alliston towards Beeton has high concentrations of methane, either in bedrock or overburden wells. This pattern is not clear in the area northeast of Alliston where bedrock wells contain high concentrations of methane, whereas in nearby overburden wells no gas was observed. No CH_4 was found in overburden and bedrock wells sampled southwest of Alliston.

Table 1 also lists data on dissolved organic carbon (DOC) in the groundwater. A correlation seems to exist between the DOC and CH_4 concentration. High DOC are accompanied by high CH_4 concentrations. Typical DOC concentrations are less than 1 ppm in deep groundwater (Thurman, 1985), and less than 5 ppm in unconfined aquifers in the Alliston area (Wassenaar et al, this volume). These higher DOC concentrations in the Alliston aquifer complex suggest that the groundwater is moving through aquifer materials that are rich in organic matter.

4.2 Isotope analyses

Environmental isotope analyses have been performed by mass spectrometry on methane (^{13}C) and groundwater samples (^{18}O and ^{2}H). The isotope data is expressed in δ o/oo units*. This data is reported in Table 2.

The $\delta^{13}C$ values for methane samples varied between -69 o/oo to -84 o/oo with most of the values around -75 o/oo. No significant isotopic differences have been noted in methane from overburden and bedrock wells. This data is similar to that reported from some overburden wells by Barker and Fritz (1981). Figure 5 shows the $\delta^{13}C$ distribution of methane gases of different origin. This figure does not include the $\delta^{13}C$ values for methane generated in landfill environments, which range between -38 o/oo to -56 o/oo for ^{13}C. All methane results from the Alliston groundwaters plot in the field of biogenic methane.

Stable isotope analyses were also carried out on some overburden and bedrock groundater. This data shows an isotopic range between - 14.3 o/oo and -10.7 o/oo for ^{18}O, and -92 o/oo and - 78 o/oo for ^{2}H. This significant isotopic difference implies that at least two types of groundwater are present in the aquifer. The isotopic composition of modern water in unconfined, shallow aquifers in the Alliston area ranges between -10.8 o/oo and -11.5 o/oo for ^{18}O and -78 o/oo and -81 o/oo for ^{2}H (Wassenaar et al, in preparation). Thus, the presence of isotopically depleted groundwaters ($\delta^{18}O$ = -14.3 o/oo) suggest that these waters were recharged under cooler climatic conditions than today.

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* δ o/oo = $R_s / R_{st} - 1$ * 1000 , where R_s and R_{st} are the isotope ratios ($^{13}C/^{12}C$, $^{18}O/^{16}O$ and $^{2}H/^{1}H$) for the sample and the standard respectively. The international standards used as a reference are PDB (Pee Dee Belemnitella) for ^{13}C and SMOW (Standard Mean Ocean Water), for ^{18}O and ^{2}H.

The preliminary isotopic data gathered suggest that the methane is biogenic in origin and is produced either in the bedrock and/or in the deep overburden materials. Radiocarbon (^{14}C) dating of methane and DOC will provide more information to better define the carbon source for the generation of methane. Major occurrences of methane seem to be found in areas underlain by limestone rocks. However, a bedrock well (386 feet) tapping shale shows the highest level of methane. The relationship between the presence of methane and the nature of the underlying bedrock will be fully tested once the methane distribution in the aquifer is better known.

5. Future work

The main goal of the first stage of this study is to determine methane distribution in the Alliston aquifer complex. Gas and water samples for isotope analyses are also being collected during this stage. Subsequently, selected wells representive of the different geochemical environments that exist in the study area will be used for a complete geochemical evaluation of the following parameters : ^{14}C and ^{13}C in methane, DOC, and DIC; ^{18}O, ^{2}H (methane) and chemistry of the groundwater. Attempts will also be made to study the potential of the kerogen present in the bedrock shales as a carbon source for methane producing bacteria. We will also examine the possibility that methane generation in some parts of the Alliston aquifer complex could be limited by the presence of sulfate-reducing bacteria. Sulfur-34 (^{34}S), a stable sulfur isotope, will be used as a tool to approach this question.

The geochemical information generated from this study will be combined with existing geological and hydrological information to postulate an acceptable theory about the origin and occurrence of methane in the Alliston aquifer complex.

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Table 1. Chemical composition of gas and DOC in water samples, Alliston aquifer complex

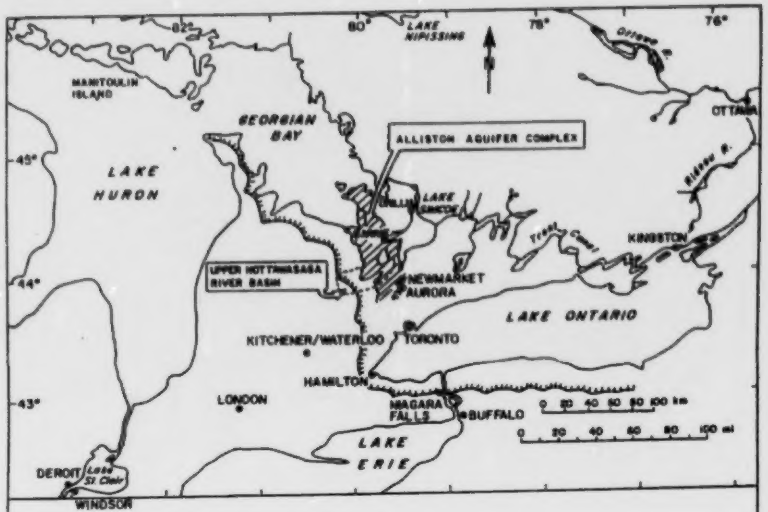
Well	Depth	CH_4	N_2	O_2	CO_2	CH_4	N_2	DOC
	ft	%				umol/l		ppm
BR*	198					<20	1180	1.4
OV**	136					<20	1055	3.2
BR	80					<20	1140	0.9
OV	177					<20	800	6.2
OV	55					1455	698	4.2
OV	122					<20	1148	2.0
OV	162					360	750	2.7
OV	176	71.9	27.4	0.50	0.85	2080	510	7.4
OV	234					<20	217	3.3
BR	320	44.2	45.8	7.63	3.70	1515	193	12.6
OV	258					<20		
BR	386	87.8	8.25	0.14	0.91	4680	380	9.3
OV	375	79.8	17.8	0.45	1.13	3550	600	22.0?
OV	281	82.1	13.6	1.25	2.70	2765	335	8.7
BR	245	83.2	13.8	0.3	1.15	2180	248	8.2
OV	194					815	667	8.1
OV	190	71.0	29.1	0.55	0.36	2650	737	9.6
BR	305	64.5	35.5	0.80	0.44	2550	977	5.2
OV	262					<20	900	1.7
BR	355	53.1	47.2	0.81	0.18	1413		6.0
OV	367					<20	985	1.9
BR	125	61.3	34.3	3.40	0.17	2425	1000	7.1

* Bedrock
** Overburden

Table 2. Isotopic composition of gas and water samples, Alliston aquifer complex

Well	Depth ft	$\delta^{13}C$ o/oo PDB	$\delta^{18}O$ o/oo SMOW	$\delta^{2}H$
		CH_4	H_2O	
BR*	198		-12.8	-89
OV**	177		-11.5	-80
OV	234		-10.8	-78
OV	176	-76.6	-12.2	-83
BR	386	-72.2	-13.8	-100
BR	320	-68.9	-12.3	-88
OV	375	-75.8	-13.5	-92
OV	281	-72.2	-10.9	-78
BR	245	-75.2	-10.7	-79
OV	190	-79.3		
OV	262		-11.6	-80
BR	305	-82.2		
BR	355	-84.5	-14.2	-100
BR	125	-77.0	-12.4	-90

* Bedrock
** Overburden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OTTAWA
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MANITOULIN ISLAND
GEORGIAN BAY
LAKE HURON
ALLISTON AQUIFER COMPLEX
LAKE SIMCOE
Trent Canal
KINGSTON
UPPER NOTTAWASAGA RIVER BASIN
NEWMARKET
AURORA
LAKE ONTARIO
KITCHENER/WATERLOO
TORONTO
HAMILTON
LONDON
NIAGARA FALLS
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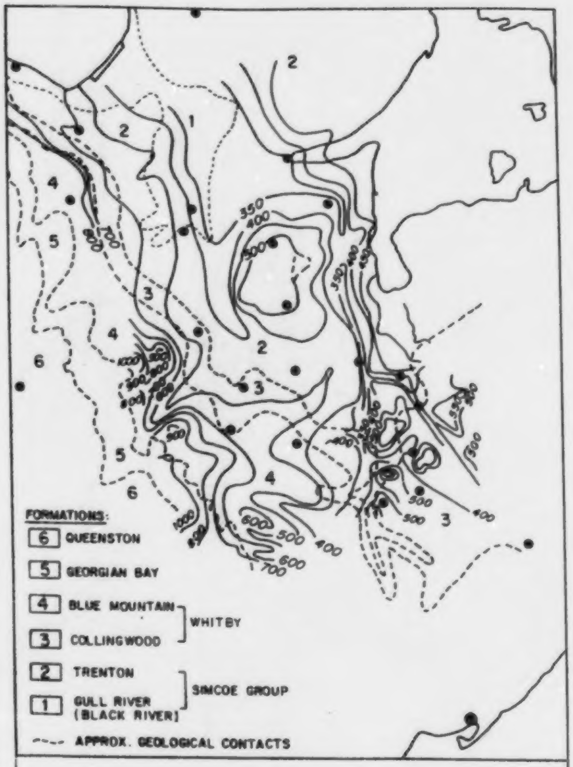
LAKE ERIE
DEROIT
Lake St. Clair
WINDSOR

Figure 1. Location map of the study area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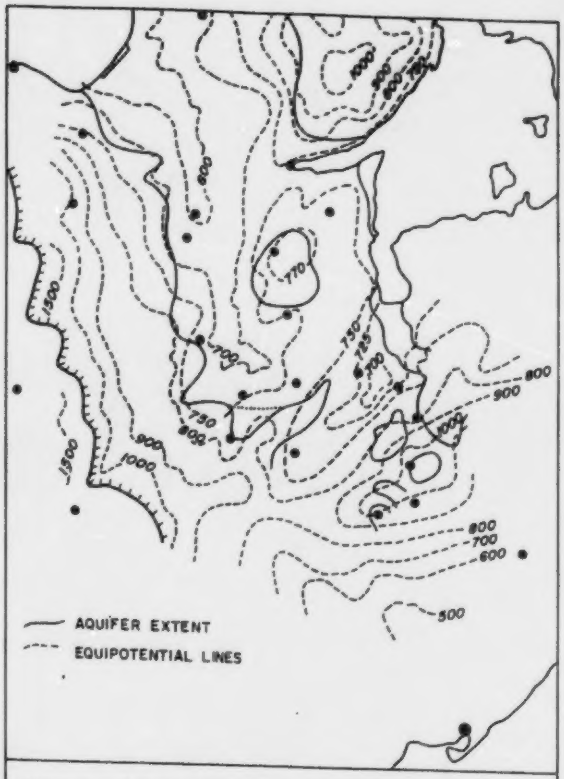
FORMATIONS:
6 QUEENSTON
5 GEORGIAN BAY
4 BLUE MOUNTAIN
3 COLLINGWOOD
WHITBY
2 TRENTON
1 GULL RIVER (BLACK RIVER)
SIMCOE GROUP
APPROX. GEOLOGICAL CONTACTS

Figure 2. Plan of bedrock topography and lithology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AQUIFER EXTENT
EQUIPOTENTIAL LINES

Figure 3: Regional Groundwater Flow Pattern

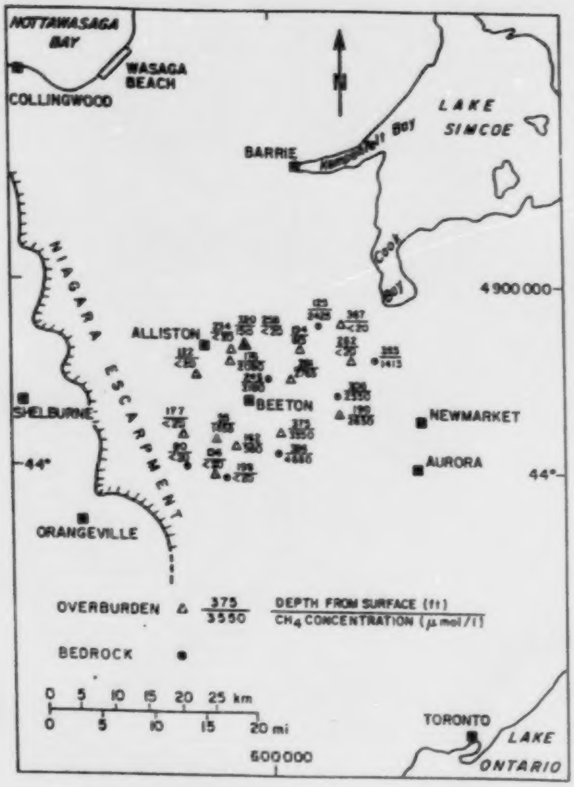
NOTTAWASAGA BAY
WASAGA BEACH
COLLINGWOOD
N
LAKE SIMCOE
BARRIE
Kempenfelt Bay
Cook Bay
4 900 000
NIAGARA ESCARPMENT
ALLISTON
BEETON
367
<20
393
1413
SHELBURNE
177
<20
NEWMARKET
AURORA
-44°
44°
ORANGEVILLE
OVERBURDEN △ 375/3550
DEPTH FROM SURFACE (ft)
CH4 CONCENTRATION (μ mol/l)
BEDROCK ●
0 5 10 15 20 25 km
0 5 10 15 20 mi
600000
TORONTO
LAKE ONTARIO

Figure 4. Sampling location and methane concentration in overburden and bedrock wells, Alliston aquifer complex.

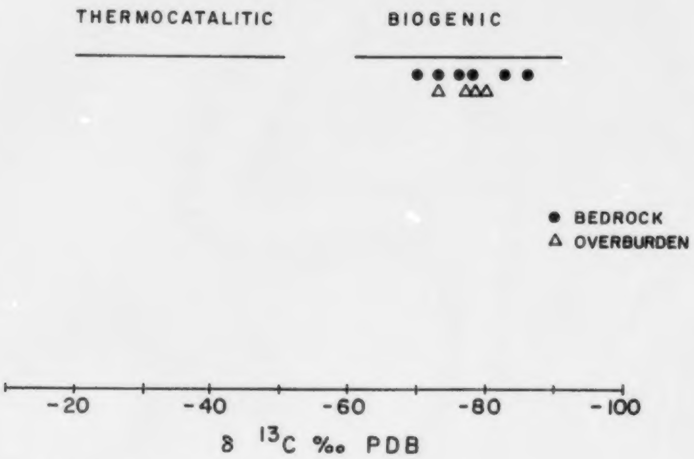

Figure 5. $\delta^{13}C$ distribution of methane of different origin and ^{13}C content in methane from overburden and bedrock wells, Alliston aquifer complex.

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The Origin, Nature and Role of Naturally Occurring Organic Solutes In Unconfined Groundwater Systems.

L.I. Wassenaar, R. Aravena, J.F. Barker, R.W. Gillham, and
P. Fritz
Waterloo Center for Groundwater Research
University of Waterloo
Waterloo, Ontario, N2L 3G1

Introduction

In recent years there has been an increasing public awareness and concern about the quality of our groundwater resources. Of particular concern is the dramatic rise in the number of toxic and resistant man-made organic chemicals identified in groundwater. These organic contaminants may enter a groundwater system from a variety of sources; landfills, disposal compounds, chemical spills, sewage, burial sites, or by the application of pesticides and herbicides in agricultural practices.

Whereas considerable effort has been spent in the detection and remediation of man-made organic contaminants in the hydrosphere, and towards the establishment of drinking water guidelines, very little is actually known of the origin, geochemistry, and role of naturally occurring dissolved organic compounds (DOC) in groundwater. In fact, relatively few studies have addressed the inherent characteristics of "natural" DOC in groundwater (Leenheer et al., 1974; Barcelona, 1984; Thurman, 1985). Several studies, however, have demonstrated the importance of natural DOC as facilitating the transport of metals (McKnight et al, 1983), enhancing the solubility of insoluble organic contaminants (Perdue, 1983), and providing a carbon source for microbial redox processes (Miller et al.,1979; Starr et al., 1987).

Objectives

The overall purpose of this M.O.E. funded two year project (1987-1989) is to determine the origin and innate characteristics of naturally occurring organic solutes in groundwater, and to define the role of naturally occurring organic solutes in the interrelated biogeochemical redox processes that affect the carbon, sulfur, and nitrogen cycles of several shallow groundwater systems in Ontario.

Origin and Nature DOC in Groundwater

Dissolved organic carbon is widespread in groundwater, although typically at concentrations below 1-2 mg C/L (Leenheer at al., 1974). High molecular weight aquatic humic substances generally account for about 20-40% of the DOC in most groundwaters (Thurman, 1985), however, the nature of the remaining 60-80% of DOC remains largely unknown. In most aquifers there are two potential sources of DOC; organic leachate translocated via aquifer recharge from the soil and vadose zone, and/or organic matter derived from kerogen originally incorporated into the aquifer sediments.

This research will attempt to characterize and describe the geochemical evolution of high and low molecular weight organic compounds that form part of the DOC along the flow paths of several shallow aquifers. Evaluation of the age, origin and residence time of DOC in groundwater will also be assessed. Methods used are liquid chromatography, molecular sieving, stable isotopic mass spectrometry, gas chromatography/mass spectrometry (GC-MS), and Tandem Accelerator Mass Spectrometry (TAMS).

Role of Natural Organic Solutes in Groundwater

In anoxic groundwater systems DOC is thought to be the electron donor for the natural remediation of several prevalent inorganic contaminants, such as fertilizer derived nitrate and acid rain derived sulfate. Denitrification and sulfate reduction can affect the carbon cycle through the oxidation of organic matter and the concomitant production of respiratory carbon dioxide. However, in order for microbes to be able to utilize DOC to reduce NO_3^- or $SO_4^=$, the carbon source must be labile. Thus, the lability of DOC must be a function of the nature of the reduced carbon forms in the groundwater system. Extensive characterization of natural DOC of several groundwater systems in this study is expected to provide insight as to the "lability" of the various fractions of DOC. High DOC concentrations in groundwater may also be linked to microbial production of methane gas (eg. Aravena et al., this volume).

In addition, oxidation of DOC during microbial redox processes could have a potentially significant effect on the bicarbonate ^{14}C dating of groundwaters, especially if the organic carbon contains little radiocarbon. Thus, a better understanding of the role of DOC in groundwater is necessary to the interpretation of groundwater ^{14}C dating.

Other aspects of this research will attempt to address the effects of dissolved organic acids and anions on routine geochemical measurements, such as pH electrode determinations and alkalinity titrations of groundwater.

Site Selection

Three unconfined sand aquifers were chosen as field study sites. At all sites the groundwater flow regimes are reasonably well known, and previous groundwater surveys at these sites provide an additional degree of information on geochemical processes in the aquifers (eg. Starr et al., 1987; Robertson and Cherry, submitted 1987).

Rodney Sand Aquifer

This unconfined, four meter thick sand aquifer underlies agricultural land near Rodney, Ontario, and comprises the glaciolacustrine sands of glacial Lake Warren. The site was used in a denitrification study by Starr et al. (1987). The water table is shallow (<100 cm), and significant concentrations of nitrate are rapidly denitrified within 50 cm below the water table. DOC in this system was presumed to be "labile", yet insufficient as the only carbon source for denitrification. The origin, fluxes, character and role of apparently "labile" DOC in this system is the focus of research.

Alliston Sand Aquifer

The unconfined, sand aquifer near Alliston, Ontario, was also used in previous denitrification studies (Starr et al., 1987). The aquifer underlies agricultural land, and is composed of glaciofluvial sands that form the present Nottawasaga River flood plain. The aquifer is hydrogeologically similar to Rodney, except that the water table occurs at a greater depth of 4 m. High levels of nitrate occur throughout this aquifer. Although DOC concentrations are similar to the Rodney site, no denitrification occurs even at 20 m depth. The origin, nature and role of seemingly "non-labile" DOC in this system is the focus of research at this site.

Sturgeon Falls Sand Aquifer

This unconfined, silty-sand aquifer is located on a forested post-glacial delta near Sturgeon Falls, Ontario.

Penetration of "bomb" produced radioactive Tritium into this system allowed for unusually accurate dating of groundwater recharge with a resolution of about 2 years spanning over 60 years of recharge (Robertson and Cherry, submitted 1987). This acid rain derived $SO_4^{=}$ which is prevalent in this system, however, undergoes dissimilatory sulfate reduction only after 16 m along the flow path (Robertson and Cherry, submitted 1987b).

The excellent hydrochemical resolution at this site is expected to yield detailed information about the temporal and spatial geochemical evolution of DOC, allow for accurate carbon mass transfer modelling, and also provide insight into the nature of carbon-sulfur cycle interactions.

Analytical Approach

All three sites have been previously instrumented with either stainless steel or PVC piezometers, spaced between 25 cm and 2 m apart. The piezometer nests are presently being sampled up to two times per year for complete water chemistry and environmental isotopes ($\delta^{18}O$, $\delta^{13}C$, $\delta^{2}H$, $\delta^{34}S$) Comprehensive geochemical measurements aid in the interpretations of basic hydrology and geochemical modelling. Statistical analysis of geochemical and DOC data will be used to test possible links between inorganic geochemistry and the organic carbon pool. Essential to DOC research in groundwater systems are a number of techniques adapted from marine and soil methods described below.

DOC Determinations

Reliable DOC determinations are essential for this study. Groundwater samples are carefully filtered through 0.45 micron filters and stored in glass vials to eliminate possible contamination. All samples are analyzed on a calibrated Dohrmann Carbon Analyzer using standard techniques.

Liquid Chromatography

XAD-8 macroporous resins are used for the isolation of the aquatic humic substances from the groundwater, for determining the hydrophobic/hydrophilic fractions of the DOC, and for classification of the DOC (cf. Thurman and Malcolm, 1981; Leenheer and Huffman, 1979). Aquatic humic substances isolated by this method are used for carbon isotope determinations (^{13}C, ^{14}C).

Molecular Sieving

Silicalite™ molecular sieve is used to concentrate the low molecular weight ($<C_{20}$) portion of the hydrophilic fraction of DOC from the groundwater. DOC isolated in this molecular sieve is then further processed for GC-MS identification and for carbon isotope determinations (^{13}C, ^{14}C).

Gas Chromatography/Mass Spectrometry

A Hewlett-Packard GC-MS is used to assist in the identification of low molecular weight organic compounds adsorbed into Silicalite. Only the 20-30 most abundant GC peaks are evaluated by computer to identify specific organic compounds.

Stable Isotope Mass Spectrometry

A Micromass(TM) 903 VG mass spectrometer for determinations of stable isotope ratios is used to measure the ^{13}C content of DOC. This technique is an excellent tool for distinguishing between marine or terrestrial derived

DOC. Stable carbon isotopic ratios are also used as a tracer of both diagenetic processes and microbial activity affecting DOC.

Radiocarbon Dating

The recent development of a Tandem Accelerator Mass Spectrometer at the University of Toronto enables radiocarbon age dating of microgram size organic samples by direct counting of ^{14}C atoms. This new technology allows age dating of very small DOC samples (5-10 mg) isolated from groundwater using XAD-8 chromatography and Silicalite. Radiocarbon ages of DOC fractions are an excellent tool for determining the origin, age, and flux of DOC in groundwater systems. Radiocarbon dating of fractions of DOC in groundwater may also be a potential tool for the age dating of groundwater (Wassenaar et al., submitted).

Potentiometric Titrations

Potentiometric titrations of humic and fulvic acids extracted from groundwater are used to quantify carboxyl functional groups and phenol functional groups.

UV Absorbance

E_4/E_6 ultraviolet absorbance ratios of aquatic humic and fulvic acids extracted from groundwater are believed to provide an indication of molecular weight of aquatic humic substances. The E_4/E_6 ratios can be compared with soil and marine humic substances.

Elemental Analyses

The carbon, oxygen, nitrogen, hydrogen and sulfur content of aquatic humic substances extracted from groundwater can be compared with those of humic substances from soils and marine environments. Thurman (1985) suggests that humic substances from groundwater contain less oxygen due to microbial action on DOC.

Preliminary Results and Discussion

Preliminary results of DOC determinations at all three sites are summarized in Figure 1 and 2. DOC concentrations in the groundwater at Rodney range between 1 and 12 mg C/L with a median of 4.6 mg C/L (Fig. 2). Generally, higher DOC contents (4-12 mg C/L) occur near the water table and decline with depth (1-1.7 mg C/L). DOC concentrations in the groundwater at Alliston range between 0.9 and 7 mg C/L, whereas, DOC in the groundwater at Sturgeon Falls ranges between 1.4 and 3.2 mg C/L (Fig. 1). These DOC concentrations are significantly higher than those observed in many deep confined aquifers (<1 mg C/L; Leenheer et al, 1974). The higher DOC concentrations in these shallow unconfined aquifers are no doubt a result of a lesser degree of biodegradation and attenuation.

DOC concentrations at the Rodney site also exhibit temporal variations (Fig 2). Whereas higher DOC concentrations occur near the water table, DOC peaks also occur below the water table. DOC peaks occur at 125 cm (12 mg C/L) and 225 cm (5 mg C/L) in April, 1988, and at 175 cm (4.5 mg C/L) for March, 1987. These peaks could represent the influx of spring or fall recharge, carrying high DOC waters leached from the soil zone. Antweiler and Drever (1983) and Cronan and Aiken (1985) have observed that higher concentrations of DOC occur in soils during spring runoff when the soil is saturated.

Starr et al (1987) measured DOC concentrations in the vadose zone from squeezed core material at this site. Their results are also summarized in Figure 2. The highest vadose/soil zone DOC values occur in the upper soil zone with a maximum value of 150 mg C/L. From 30 cm to 90 cm depth, DOC drops to between 25 and 19 mg C/L and then to less than 12 mg C/L below the water table (Fig 2). The sharp drop in porewater DOC concentrations below 5-10 cm is a result of microbial biodegradation and adsorption in the vadose zone (Dawson et al, 1981; Meyer and Tate, 1983).

Nature of DOC

Preliminary results of the two main fractions of DOC isolated from groundwater at Rodney and Alliston are summarized in Figure 3. At Rodney the amount of dissolved hydrophobics varied between 15 and 88 percent of the total DOC, and showed significant variations with depth (Fig 2). Similarly, the hydrophilic fraction also varied with depth to between 12 and 85 percent of the total DOC. At Alliston the amount of hydrophobic DOC ranges between 0 and 50 percent of the total DOC. The hydrophobic fraction of DOC in these aquifers was determined to be >95% fulvic acid.

Preliminary data from the Rodney field site suggests the amount of DOC and its fractions may be temporally and spatially variable in aquifer recharge environments due to seasonal variations associated with groundwater recharge.

Hydrologic transport, however, may account for only part of the variation in the hydrophilic/hydrophobic fraction of DOC in groundwater. In the aquifers at Rodney and Alliston the hydrophobic fraction of the DOC shows a strong correlation with the total concentration of DOC (r^2 = 0.96; Fig 3). However, the hydrophilic fraction does not correlate as strongly with total concentration of DOC (r^2 = 0.52). Thus, changes in DOC concentration observed with depth are primarily due to changes in the hydrophobic fraction, and to a lesser extent the hydrophilic fraction.

GC-MS and carbon isotopic characterization of the DOC at the Rodney site suggest that microbial processes may also be an important control over the hydrophilic fraction of the

DOC. Table 1 lists compounds that we were able to identify by GC-MS for the hydrophilic fraction. The GC-MS chromatogram indicated the hydrophilic fraction at 125 cm depth was composed mainly (estimated >95%) of very low molecular weight compounds (C_4-C_1). The largest GC peak was identified as methyl acetate. The GC-MS used was not able to positively identify smaller organic compounds, such as formate. Acetate, however, is a well known microbial by-product of anaerobic fermentation of kerogen and perhaps DOC, and is the most common volatile fatty acid found in natural waters (Miller et al, 1979; Barcelona, 1980; Thurman 1985). Interestingly, methyl acetate, as well as many other LMW compounds identified at 125 cm (DOC=12 mg C/L), are not present at a depth of 250 cm (DOC = 4 mg C/L; Table 1). We believe many of these LMW compounds may have been utilized by microbes in the zone of denitrification and sulfate reduction that occurs between 100 and 200 cm depth. LMW organic acids, and especially acetate are well known substrates for nitrate, sulfate reducing and methanogenic bacteria (cf. Cappenberg and Prins, 1974). It is possible, however, that seasonal variations in DOC recharge may also affect the types of LMW compounds entering the aquifer.

Virtually all LMW compounds identified in the hydrophilic fraction of the DOC at Rodney (Table 1) are potential degradation products of lignins, cellulose, and soil organic matter (Thurman, 1985). The two chlorinated compounds identified, however, may possibly be the result of a reaction of chlorine (from chlorinated herbicides?) and fulvic acid (cf. Oliver and Visser, 1980), and/or derived from degradation of herbicides and fertilizers applied to the field.

The data also suggest that some U.S.A. EPA rated priority pollutants (eg., toluene, benzene, xylenes) occur naturally at trace levels in groundwater, although it was not possible with the isolation method used to quantify their concentrations. Our research suggests that further data on "natural" levels of toxic organic compounds in groundwater should be obtained. A separation between "natural" and anthropogenic organic compounds may provide better criterion for the establishment of drinking water guidelines.

Carbon Isotopes and DOC

Preliminary results of $^{13}C/^{12}C$ and ^{14}C TAMS analyses of the hydrophobic and hydrophilic fractions of the DOC from the Rodney aquifer are summarized in Figure 2. Carbon-13 isotope values measured for both hydrophobic DOC samples were -27.3 °/oo and -30.5 °/oo (PDB; Fig 2). These values are similar to soil organic matter and humic substances derived from C_3-type vegetation (Deines, 1980). The $\delta^{13}C$ value of the hydrophilic fraction at 125 cm, however, has an extremely depleted value of -47 °/oo (PDB). If one assumes that the hydrophilic fraction at 125 cm is a result of microbial fermentation of particulate organic matter and/or DOC, as is suggested by the presence of methyl acetate in the sample, then microbial isotope effects may be the cause for ^{12}C enrichment in the sample. This carbon isotopic fractionation process may be analogous to the large isotope effects observed in microbial methane fermentation (cf. Deines, 1980; Barker and Fritz, 1981).

A loss of ^{12}C enriched LMW acids is evident below the nitrate and sulfate reduction zone at Rodney. At 250 cm depth only larger molecular weight $(>C_6)$ organic compounds were identified and the sample had a $\delta^{13}C$ value of -24.0 °/oo, which is similar to that of the precursor C_3 plant matter (Deines, 1980). It is possible that LMW organic compounds, such as acetate or formate, are preferentially utilized by nitrate and sulfate reducing microbes in groundwater.

Radiocarbon data for the hydrophobic and hydrophilic fractions of the DOC at Rodney are also summarized in Figure

2. The results indicate significant differences in ^{14}C activity between hydrophobic samples collected at 125 and 250 cm depth. (NOTE: ^{14}C activity is usually expressed as percent modern carbon- PMC, or as a conventional age in years before 1950 - B.P.) Substantial differences in ^{14}C activity are also observed between the hydrophobic and hydrophilic fractions. The hydrophobic fraction at 125 cm has a ^{14}C activity of 91.8 PMC (600 years B.P.), but has only 76 PMC (2,200 years B.P.) at 250 cm (Fig 2). Clearly, the hydrophobic fraction at 125 cm (91.8 PMC) must originate from the upper soil profile when compared to the ^{14}C activity of humic substances extracted from a core, which are only 79 PMC (1,910 years B.P.) at a depth of 30 cm (Fig 2).

Considering the hydrology of the Rodney aquifer, the reduction in ^{14}C activity of the hydrophobic fraction cannot represent the advective residence time between 125 and 250 cm. Two theories may account for this lower ^{14}C activity of the hydrophobic fraction at 250 cm. One possibility is that the hydrophobic fraction of the DOC is a mixture of young carbon from the soil zone and older components from the sediments, the latter being more significant at depth. This mixing of young and older humic substances may be seasonally variable. However, one can also argue that perhaps a "younger" (and more labile?) component of the hydrophobic fraction of the DOC is being preferentially consumed by microbes. It is generally believed that humic substances and aquifer kerogen, due to their refractory nature, are not a readily available carbon source for microbes. If this is true then the addition of large molecular weight humic substances from aquifer organic material would not account for the observations.

A second possibility is that the ^{14}C activity differences of the hydrophobic fraction in the aquifer as a whole simply reflect temporal differences in the ^{14}C activity of DOC entering the aquifer from the vadose zone (ie, spring DOC flux vs. fall recharge). In this respect it is interesting to note that the lower ^{14}C-DOC activity at 250 cm depth is paralleled by a $\delta^{18}O$ value of the water near -11 $^{o}/oo$ reflecting winter/spring recharge, whereas the sample collected at 125 cm has a $\delta^{18}O$ value near -8 $^{o}/oo$ reflecting summer/fall recharge.

The ^{14}C activities of the hydrophilic fraction are significantly lower, 67-69 PMC (2930-3280 years B.P.), than the hydrophobic fraction and are similar for both samples (Fig 2). This requires a significant input of old carbon to the hydrophilic fraction of the DOC.

We have identified a large component of LMW organic acids for the sample at 125 cm at Rodney (Table 1). The presence of methyl acetate, and possibly the ^{12}C enrichment, may indicate this fraction of the DOC contains a significant amount of organic solutes derived from microbial fermentation of kerogen and/or DOC. This fraction does not correlate strongly with total amount of DOC (Fig 3), which has been shown to vary seasonally, and is generally present in concentrations of less than 2 mg C/L. The similarity of the ^{14}C content of the hydrophilic fraction of the DOC and the carbon in the solid phase (Fig 2) seems to suggest a direct link between the two components.

Current Research

Completion of field research and data analysis will comprise the final year of this project (1988-1989). Our immediate goals are;

1. to complete isolation of natural DOC at Alliston and Sturgeon Falls for geochemical analyses,
2. to complete isotopic and GC-MS analyses of DOC at Alliston and Sturgeon Falls sites,
3. to complete detailed characterization of aquatic humic substances from all three sites,

3. to identify redox processes that utilize DOC and affect the C, S, and N cycles of these aquifers,
4. to present a cognitive model for the origin and age of natural organic solutes in different groundwater regimes, and,
5. to present a quantitative geochemical model for the evolution and mass transfer of DOC in groundwater flow systems.

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Table 1. GC-MS identified dissolved hydrophilic compounds from Rodney sand aquifer. Samples were thermally desorbed from silicalite molecular sieve.

R3-1 - 125 cm	R3-6 - 250 cm
Dominant Compounds	
methyl acetate	none
Minor Compounds	
toluene	n-hexane
hydroxylamine	p + m xylenes
chloroform	cyclohexane
2-ethyl-1-hexanol	cyclopentane
p + m xylenes	stearic acid
diphosphoric acid, diisooctyl ester	palmitic acid
1,2-dichloro-benzene	
2-methyl propanate	
2,6-dimethyl-nonane	
benzene	
ethyl benzene	
benzoic acid, methyl ester	

List of Figures

Figure 1. Concentrations of natural organic solutes in two unconfined sand aquifers of Ontario. Triangles denote the Alliston site, and squares denote Sturgeon Falls field site.

Figure 2. DOC concentrations, percentage of hydrophobic and hydrophilic fractions of the DOC, weight percent organic solids, 14C activity and 13C (PDB) isotope values of DOC and organic solids from the Rodney sand aquifer. Sampling times are denoted by; □ - January, 1987, ○ - March, 1987, △ - June, 1987, * - April, 1988. Vadose zone data (▲) and weight % organic solid determinations (●) from Starr et al (1987). Note upper scale for vadose zone DOC concentrations. See preliminary discussion of data for details.

Figure 3. Correlation of the hydrophobic and hydrophilic fractions of DOC with total DOC concentration. Based on combined data from the Rodney and Alliston sand aquifer.

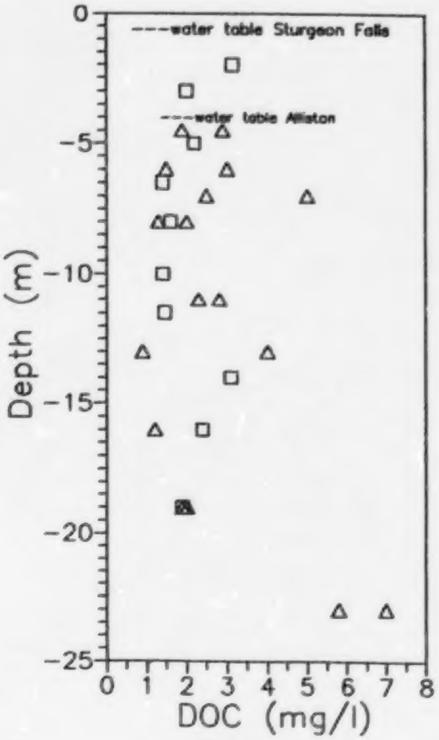

---water table Sturgeon Falls
---water table Alliston
0
-5
-10
-15
-20
-25
Depth (m)
0
1
2
3
4
5
6
7
8
DOC (mg/l)

Figure 1

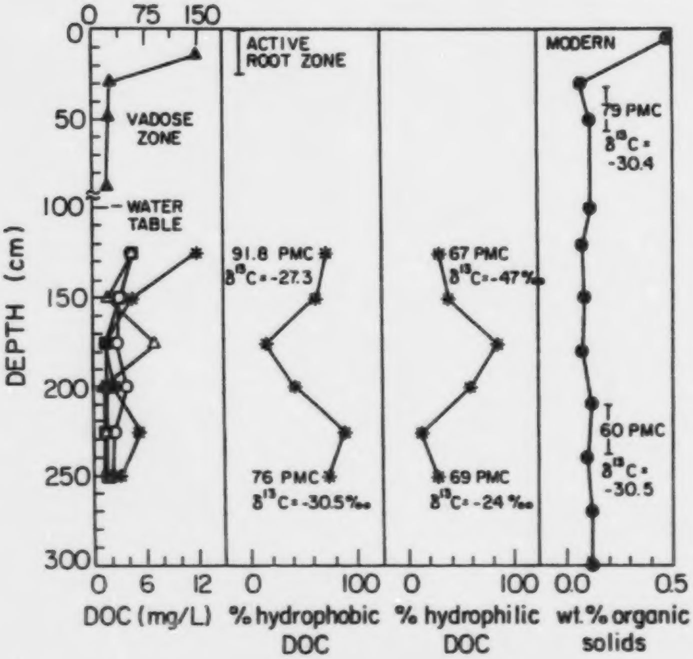
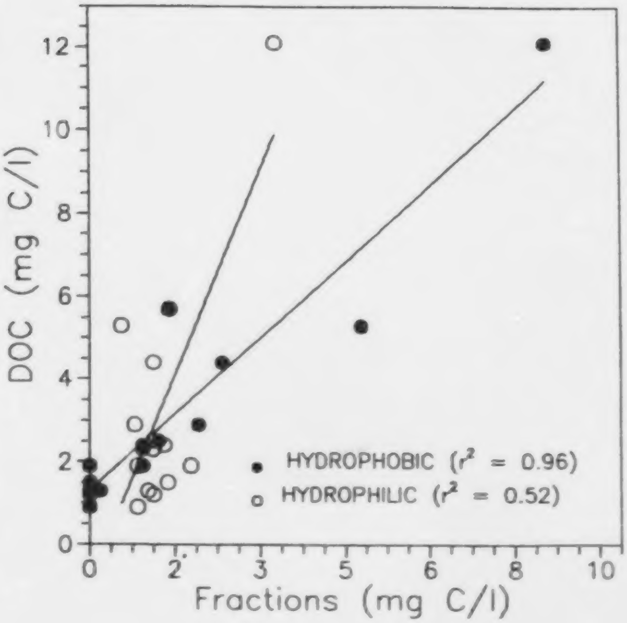

0
75
150
0
50
100
150
200
250
300
DEPTH (cm)
VADOSE ZONE
WATER TABLE
ACTIVE ROOT ZONE
91.8 PMC
δ13C=-27.3
76 PMC
δ13C=-30.5‰
67 PMC
δ13C=-47‰
69 PMC
δ13C=-24 ‰
MODERN
79 PMC
δ13C= -30.4
60 PMC
δ13C= -30.5
0
6
12
DOC (mg/L)
0
100
% hydrophobic DOC
0
100
% hydrophilic DOC
0.0
0.5
wt.% organic solids

FIGURE 2



DOC (mg C/l)
0
2
4
6
8
10
12
HYDROPHOBIC (r^2 = 0.96)
HYDROPHILIC (r^2 = 0.52)
0
2
3
5
6
8
10
Fractions (mg C/l)

Figure 3

C10

STUDY OF IN PLACE POLLUTANTS IN THE TWELVE MILE CREEK
AND
WELLAND RIVER

by
Ian Brindle, Anne Wei-chu, Xing-fang Li and
Cindy L. MacLaurin

Chemistry Department
Brock University
St. Catharines, Ontario L2S 3A1

Introduction

Industrial activity inevitably generates by-products that can, if uncontrolled, create environmental problems. Thus coal burning for power generation, coke production, or domestic consumption, gives rise to fly ash that contains polynuclear aromatic hydrocarbons (PAHs) and elevated levels of heavy metals. The fallout from such activities can raise the levels of these contaminants in surrounding soils and sediments. Process water for industry can become contaminated with the products or by-products of that industry and hence, at the outflow of the industry, this water can become a point-source of contamination. PCBs appear in the environment because of accidental spills from the manufacture or destruction of transformers and from the use in formulations in printing inks, cutting oils, lubricating oils, etc.

PAHs

Polynuclear aromatic hydrocarbons (PAHs) are associated with soot and tar materials. They are adventitious products of pyrolysis of carbon-rich materials and have the dubious reputation of being a major component of the first identified carcinogenic material. Thus soot was identified in the eighteenth century as the cause of scrotum cancer among chimney sweeps[1].

Since their identification as hazardous materials, much work has been done to identify the mode of action and the relative carcinogenicity of the many components of PAHs. PAHs at high concentrations in sediments have given rise to tumour formation on the lips of bottom feeding fish. Also, PAHs can be transferred from sediments to the fatty tissues of shellfish, crustaceans and fish. Thebiomagnification effect may make concentrations of PAHs sufficiently high in the adipose tissues of fish to give cause for concern if these fish were to be eaten.

Heavy Metals

Metal processing industries have inevitably produced wastes that are contaminated with metals and acidic materials. Thus fly-ash from smelting can contain volatile metals such as arsenic and tin as well as, for example, iron. Process water can become contaminated with metals which co-precipitate with hydrated iron oxides.

An element of particular concern in the aqueous environment is nickel. Concentrations of nickel as low as 5-10 $\mu g\ L^{-1}$ have exterminated Daphnia species within three generations[2]. The effects on embryonic stages of the rainbow trout (salmo gairdneri) indicate that the LC_{50} value is as low as 50 μg/L. Different species show different sensitivities, the lowest fish sensitivity may be in the common gold fish (carassius auratus) whose LD_{50} is 2.8 mg L^{-1} [3].

The use of nickel in specialty steels makes nickel a potential pollutant from steel making industries such as Atlas Steels. Other elements such as chromium, cobalt and zinc would be considered less problematical from an environmental toxicological standpoint. Although chromium in its +6 oxidation state is a serious hazard, this is usually derived from metal finishing industries, where dichromate is used in plating baths[4].

PCBs

The polychlorinated biphenyls were manufactured on a substantial scale between 1930 and 1970. The major uses for these compounds were transformers and capacitors, but they were also used in lubricating oils, printing ink formulations, plasticisers and as additives in petroleum products.

The discovery of PCBs in fish and the accidental contamination of rice oil in Japan in the late 1960s led to a voluntary ban on the use of PCBs in 1970. These regulations have been tightened up since this time and control over PCB transportation is now highly regulated.

Thermal treatment of PCBs can lead to the formation of polychlorinated dibenzofurans (PCDFs), whose toxicological properties parallel the polychlorinated dibenzodioxins. Thus transformer shorts and low temperature incineration of transformers (such as might occur in scrap metal yards) can lead to the production of PCDFs[5].

Description of Work to Date

PCBs

Sediment samples were acquired from a number of locations. The PCB study involved samples taken from the 12 Mile Creek and tributaries, from Martindale Pond and from the Welland River and tributaries. Fish samples were also acquired from as many locations as possible. The expectation was that biomagnification could lead to increased levels of PCBs in fish tissue and this might point to locations of high concentration. A variety of species of fish were taken to see if there was any variation in the concentrations of PCBs. Locations of sediment samples and results are shown on maps 1, 2 & 3 and in Table 1. Fish sample results are shown in Table 2.

Results to date for sediment samples and for fish show levels of PCBs below our level of quantitation, usually not detectable. Quality assurance checks with M.O.E. labs in Rexdale, analysis of a lake trout taken from the Niagara River and analysis of the sediment reference material from CCIW showed our methodology to be adequate for the extraction and quantitation of PCBs down to a concentration of 100 ppb.

Chlorinated Pesticides

Since chlorinated pesticides tend to interfere with the analysis of PCBs, these compounds were separated by chromatography in all samples that were also analysed for PCBs. Unfortunately, sulfur proved to be a problematical interference in the determination of aldrin, thus results for aldrin have been removed. The analysis for the remaining pesticides is listed in Tables 1 & 2.

TABLE 1

PCB ANALYSIS ON SEDIMENT SAMPLES

SAMPLE SERIES	SAMPLE #	LOCATION	RESULTS FOR PCB'S *
12 Mile Creek #1	1	Old Welland Canal South Side	n.d.
12 Mile Creek #1	2	Old Welland Canal East of junction South side	n.d..
12 Mile Creek #1	3	Old Welland Canal 100 m West of old bridge Glendale Ave.	n.d.

12 Mile Creek #1	4	Old Welland Canal North side 200 m East of junction	n.d.
12 Mile Creek #1	5	Old Welland Canal South of Weir East side	n.d.
Eastchester	1	At landfill outfall	n.d.
Eastchester	2	East stream at footbridge, adj. to Oakdale Ave.	n.d.
Eastchester	3	Old Welland Canal at 406 Geneva cut-off 0-5 cm deep	<100 ppb
Eastchester	4	Old Welland Canal at 406 Geneva cut-off 5-10 cm deep	<100 ppb
Eastchester	5	Adj. to Domtar outfall Old Welland Canal at Walker's Mile	n.d.
B.F. Goodrich	1		n.d.
B.F. Goodrich	4		n.d.
B.F. Goodrich	7		n.d.
12 Mile Creek #2	1	Old Welland Canal Southside 0-5 cm deep	n.d.
12 Mile Creek #2	2	Old Welland Canal Southside 5-10 cm deep	<100 ppb
12 Mile Creek #2	3	Upstream of Weir at Old Welland Canal	n.d.
12 Mile Creek #2	4	At 406	n.d.
12 Mile Creek #2	5	South end of G.M. plant	n.d.

12 Mile Creek #2	6	At north end of G.M. plant	<100 ppb (hydrocarbons)
Martindale Pond	1	South-west side Martindale road	n.d.
Martindale Pond	2	North end at Port Dalhousie House	n.d.
Martindale Pond	3	At Seaplane Dock	n.d.
Martindale Pond	4	West side, Henley Island	n.d.
Welland River	1	Reef, Atlas Steel's outfall	n.d.
Welland River	2	Reef, Atlas Steel's outfall (organic rich)	<100 ppb
Welland River	3	Thompson's Creek at Chippawa Creek Rd.	<100 ppb
Welland River	4	Lyon's Creek at Willodell Rd.	n.d.
Welland River	5	Tea Creek at Willodell Rd.	sample destroyed while being processed
Welland River	6	Grassy Bank Creek at Morris Rd.	n.d.
CCIW Sediment standard		quantified	1.44 ppm
12 Mile Creek	X1	Adjacent to bridge Glendale Ave	n.d.
Sucker Creek	X2	At Welland River	n.d.
Welland River	X3	At Regional Rd. #24	n.d.
Beaver Creek	X4	At Welland River	n.d.

* n.d. - not detected

TABLE 2 WELLAND RIVER FISH

Name	Location	PCB *	Organochlorine *
Rock Bass (2) *Ambloplites rupestris*	Atlas Steels	1. n.d. 2. <0.100ppm	1. n.d. 2. DDE 0.16 ppm
Smelt *Hypomesus Olidus*	Atlas Steels	<0.100 ppm	chlordane 0.04 ppm
Bluegill sunfish *Lepomis macrochirus*	Atlas Steels	n.d.	n.d.
Sheephead *Archosagus probatocephalus*	Atlas Steels	<0.100 ppm	chlordane 0.09 ppm DDE 0.17 ppm
Emerald Shiner *Notropis atherinoides*	25 m downstream from Atlas-Mansfield sewer	<0.100 ppm	chlordane <0.02ppm
Gizzard Shad *Dorosoma cepedianum*	Immediately downstream of B.F. Goodrich plant	<0.100 ppm	chlordane <0.02ppm
Golden Shiner *Notemigonus crysoleucas*	Immediately downstream of B.F. Goodrich plant	n.d.	n.d.
Emerald Shiner(2) *Notropis atherinoides*	Immediately downstream of Thompson's Creek	1. n.d. 2. <0.100 ppm	1. chlordane <0.02 ppm 2. DDE 0.17 ppm -BHC 0.03 ppm
Emeerald Shiner *Notropis atherinoides*	Emerson Bridge	<0.100ppm	chlordane <0.02ppm
Golden Shiner *Notemigonus crysoleucas*	Welland Airport	n.d.	DDE 0.12 ppm chlordane 0.04 ppm
Carp *Cyprinus carpio*	Lake Gibson	n.d.	n.d.
Carp/Goldfish hybrid *Cyprinus carpio/ Carassius aureatus*	Lake Gibson	n.d.	n.d.

Channel Catfish *Ictahirus* *punctatus*	Lake Gibson	n.d.	n.d.	
Brown bullhead *Ictalurus* *nebulosus*	12 Mile Creek K-mart Plaza St. Catharines	<0.100 ppm		chlordane <0.020 ppm

* n.d. - not detected

Survey Scans

A number of samples were analysed by GC/MS to determine the nature of contaminants, other than PCBs and chlorinated pesticides.

The complex nature of some of the oily sediments in the 12 Mile Creek and Welland river made analysis difficult, due to the extremely large numbers of peaks. Some success was achieved with the 12 Mile Creek sediments taken from the confluence with the Old Welland Canal, below St. Paul Street in St. Catharines. The compounds identified include a number of long chain alkyl benzene congeners with ten to twelve carbons in the chain. Also identified were diethylbiphenyl, dimethylbiphenyl, hexaethyl benzene, and p-terphenyl, any of which could be associated with transformers as cooling agents. Phenolic compounds, most likely resulting from lignin degradation in the processing of wood pulp were also present.

In contrast to the 12 Mile Creek, the Welland River proved to be much more complex. Essentially every sample taken from the Welland River downstream from the city of Welland contained polynuclear aromatic hydrocarbons. This finding is consistent with the observations reported by E.G. Adamek in a report for the Ministry of the Environment, published in 1976. In this report high levels of benzo-[a]-pyrene and benzo-[k]-fluoranthene were reported in the air downwind of major manufacturing facilities in the city of Welland. The fallout from these activities would accumulate in the sediments of the

Welland River which flows almost directly along the path of the prevailing wind. In parallel work funded by the World Wildlife Fund, or sediment near the B.F. Goodrich plant has shown a slightly positive SOS chromotoxicity test when activated by S9 liver microsomes[6], suggesting that this Welland River sediment may be mutagenic. We have developed a GC method for the determination of PAHs that appears to improve the detection limit for late-eluting PAHs. We felt that this would be important in our determination of the more toxic PAHs such as benzo-[a]-pyrene in the Welland River. This method is currently being prepared for publication.

The B.F. Goodrich plant on the Welland River makes polyvinyl chloride and several other vinyl polymers. These polymers are produced by emulsion polymerisation in aqueous solutions containing detergent. Sodium lauryl sulfate is the major detergent used in this process. The treatment of waste waters from the polymerisation process produces an effluent that flows into the Welland River. Inspection of the outfall from B.F. Goodrich showed that the sediment and pebbles on the bottom of the river adjacent to the outfall were coated with algal organisms. The analysis of the sediment showed the presence of long chain, typically C_{12}, alcohols. Alkyl sulfonates would likely hydrolyse to the corresponding alcohols during the water treatment process. This rich, readily metabolised carbon source is probably responsible for the rich algal growth.

A curious series of samples were obtained from the area of the Ford Glass plant, which is close to the Queen Elizabeth Way. The appearance of a series of peaks in the GC/MS scan with virtually identical mass spectra corresponding to a polynuclear aromatic compound (in this case either anthracene or phenanthrene) but carrying a C_6H_{13} moiety somewhere on the nucleus. Again, there were a number of peaks with the same formula weight and basic mass spectral fragmentation pattern which suggested a series of congeners. As with other congeners, the temptation is to think that these compounds are the products of a chemical synthesis rather than the adventitious products of a combustion process. Whereas methyl, or even dimethyl polynuclear aromatic compounds can be formed from pyrolysis of carbonaceous materials, it seems very unlikely that a series of congeners containing an unusual C_6H_{13} group would survive such a process.

Inorganic Survey

Because of the visible plumes of iron-rich material and elevated conductivity levels, Atlas Steels outfall was investigated to determine if levels of toxic elements were accumulating. Levels of cobalt, copper, lead, nickel and zinc were high in the reef that was formed around the outlet from the Atlas Steels plant.

Collaboration with Niagara River Improvement Team

At the request of Jack Viirland and Mike Jovanovich of the NRIT we set up a series of extractions of effluents from a number of industries and sewage treatment plants discharging directly or indirectly into the Niagara River. Analysis provided some interesting information to that group. Scans were run to determine if other compounds were being missed in the normal scan. In fact, morpholine, a compound which is used to descale boilers, appeared as a significant peak in several effluents from industries - no doubt from boiler blow-down. Compounds identified as purines were also found in some of the effluents leading to the conclusion that sewage from the plant was not always being directed to the sewage treatment plant. The appearance of methyl phthalate in the effluent of the Fort Erie (Anger Ave) sewage treatment facility confirmed the Ministry's detection of this compound in the effluent.

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Ongoing Work

Although no PCBs were found in the top 10 cm of sediment in the Old Welland Canal, persistent stories of PCBs being dumped into the old canal suggests that a deeper core from the old canal may provide evidence of this dumping. At the present time there are thick organic (wood fibre?) sediments in the lagoon-like area of the old canal. If the sedimentation has been rapid, the accumulated sediment may be covering any PCBs that were dumped, say, twenty to thirty years ago. Because the sediments contain a considerable hydrocarbon fraction, GC/MS with selective ion monitoring will be necessary to determine PCBs in such a mixture. Samples of this sediment, down to the limits of retrieval of a Livingstone sampler (1.1 meter in this case), are currently being analysed in our laboratory.

Atlas Steels had controlled much of its emissions of iron rich material. However, because it is a collector of other metals, the flocculent hydrated iron oxide still discharged from Atlas Steels is being analysed to determine if this material can act as a carrier of toxic metals into the ecosystem. After the determination of metals available by nitric acid treatment, leaching determinations will be made to determine the availability to organisms. The extent of migration of the metals from the Atlas Steels outfall is being mapped to provide information and to help in any decisions that will be made with respect to possible remedial action. The polynuclear aromatic hydrocarbons in the Welland River are being determined and the levels of these compounds in the system will be mapped. This will be an interesting study that should show the relationship between the likely source of the material in Welland and its distribution in the river as a result of aerial distribution and sediment transport.

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RESEARCH AND DEVELOPMENT OF PERMANENT ONSITE SOLUTIONS FOR CONTAMINATION OF GROUNDWATER AT WASTE DISPOSAL AND INDUSTRIAL SITES IN CANADA

Richard J. Rush
CANVIRO Consultants, A Division
of CH2M HILL Engineering Ltd.

This paper consists of an overview of a recently-awarded two-year project to research, develop and demonstrate permanent onsite solutions for groundwater contamination, specifically contamination attributable to toxic organic chemicals. The Uniroyal Chemical Manufacturing Plant in Elmira, Ontario has been selected as a demonstration site for the methods developed. The project is being conducted in conjunction with Morrison-Beatty Limited, and it is being funded by the Department of Supply and Services, the Ontario Ministry of the Environment and Uniroyal.

Phase I of the project will include a technology update (ie. literature review) on groundwater treatment methods, screening of treatment technologies, laboratory and pilot scale studies on groundwater and soil samples from the Uniroyal site, the development of a hydrogeological management model for assessing recovery and injection well networks, and preliminary design work for the selected technologies.

Phase II of the project will consist of field scale demonstrations of selected technologies. In situ purge well testing followed by treatment of groundwater at surface (ie. air stripping with off-gas treatment, granular activated carbon) have been identified for possible implementation. A comprehensive evaluation will be made for each of the demonstrations performed, and where possible, recommendations will be made regarding the applications of these technologies at other industrial and waste disposal sites with groundwater contaminated with organic chemicals.

Because this project has just been started, no results are available to present in written form for this conference.

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THE ROLE OF GRONDWATER IN HUMAN SOCIETY

R.N. Farvolden
Waterloo Centre for Groundwater Research
University of Waterloo
Waterloo, Ontario.
N2J 4H8

In this presentation I want to show that groundwater involves more than a supply for a farm or cottage well but is an important factor in many geological phenomena as well as being a major component of stream flow and storm runoff. It has been, and is, a major factor in human societies. We have many examples of grave social problems that have their roots in poor planning or poor understanding or poor decisions in groundwater matters.

First, I want to refer to several technical matters that will remind you of the importance of groundwater in some phenomena that do not impact on our daily lives.

After many years of mainly qualitative or descriptive analyses of regional groundwater flow, Hubbert, in 1940, showed that this problem was amenable to analysis by potential- field methods used by physicists and mathematicians. His concepts were not well received at first by the people working in groundwater, probably because his assumptions or generalizations did not match those of classical hydrogeology. Twenty years later, Joe Toth, Alan Freeze and Paul Witherspoon applied computer analysis to field studies to demonstrate the validity of Hubbert's gravity flow system concept. Freeze went on to incorporate all subsurface flow into an analysis of the runoff cycle and and Toth has found very interesting relations between regional groundwater flow and oil pools. Reference to groundwater flow systems has become a trademark of field studies by Canadian hydrogeologists.

As long ago as 1960 Hubbert and Rubey published a pair of papers on the role of groundwater in overthrust faulting. They concluded that the only mechanism that could account for these great displacements (dozens of kilometres) by mountain-sized blocks of rock, was gravitational sliding on planes of excess pore- water pressure. They went on to show this situation could have existed during the time the faulting occurred.

In 1966, Evans described the "Denver Earthquakes" as caused by injection of liquid wastes in Precambrian rocks at a depth of about 3000m. Now Bredehoeft and his colleagues at the U.S. Geological Survey in Menlo Park, California, can cause earthquakes in Wyoming by sending commands to start deep- well injection.

These examples may seem very far from our normal concerns so I want to turn to groundwater in the sense that we usually deal with it- in the runoff cycle or in wells.

For his M.Sc. research at Waterloo, Mike Sklash used environmental isotopes (oxygen-18 and deuterium) to show that in small streams, storm sunoff is comprised mainly of groundwater. We all knew that base- flow was entirely groundwater- in southern Ontario it is about 40% of total stream discharge- but we did not expect to find so much of it in storm runoff. For his Ph. D. thesis Sklash showed this to be the rule in all basins he studied in Canada, and he proposed a mechanism to account for it. The idea is hard to accept but the results are hard to refute. One wonders why it has never been considered in routine engineering hydrology work. I offer three possibilities: 1) engineering hydrologists don't know about the work or don't believe the results; 2) it is not important in runoff modeling or analysis; or 3) it hasn't appeared in standard texts used in engineering schools.

Both flood water and storm flow have been important in human society since the dawn of civilization. I'd like to convince you by conjectures, that groundwater conditions of these earliest irrigation operations eventually led to the downfall of the society. We might think of it as the first social disaster caused by neglecting groundwater in operations and planning.

The favoured places for irrigation using floodwaters were, and are, the flat lowlands of rivers and lakes plains, where the alluvial surface is flat and gently sloping.The soils are rich, and water is easily delivered to the fields. The agricultural society that first developed along the Tigris and Euphrates rivers thrived, in part we know, because of such favourable conditions. But the society eventually failed and students of ancient history commonly include water problems as one of the causes. In no case I know of do the historians consider the fact that the groundwater flow system may have been an important contributor to deteriorating conditions in the cultivated fields. The link is pretty obvious if we think about it. Surely, the irrigated fields were in a zone of groundwater discharge. We can assume this with some confidence merely from descriptions of the terrane- low-lying land adjacent to rivers. Normal evapotranspiration of the water by the crops would cause slow accumulation of salt and salinization would eventually become a serious problem. The common practise of flushing out the salt by using excessive application of irrigation water would not work because, being in a discharge zone, the upward groundwater gradient would would prevent downward drainage. Instead of flushing, there would be water- logging. Similar circumstances are noted in many major irrigation schemes of the past and present. According to Barney "worldwide an estimated 125,000 hectares of irrigated land are lost from production each year due to waterlogging, salinization, and alkalization."

Now I want to turn to the aspects of groundwater that we know best..water supply. Springs and streams with good base flow were and are, the favourite sites for human settlement. We note that if the supply is small, problems are few. People adapt their needs to what is available. In an extreme case, a small tropical island of carbonate sand is home to several families. Before setting foot on the island we can assume that a lense of fresh water occurs in the porous sand, floating on saline ocean water, with a recharge- discharge regime like that proposed by Hubbert. The inhabitants can get water from shallow pits, and as long as they use only fresh water that is about to be discharged into the sea, they have a secure supply. A similar condition occurs on a larger, neighbouring island. Here, discharge occurs in a contact spring, and the inhabitants have a secure supply. The City of Kupang, Indonesia, a few kilometres away, was established and grew around similar springs. Surface water is almost non- existent.

because of the highly permeable limestone. Now, less than 50% of the inhabitants are served by the water system, and those get service less than 50% of the time. Improvement of the system is planned, so that some 80% of the people will have a continual supply of water. The question then is, how much groundwater is available? Surface water sources are far away and even then, reservoir sites are either on the cavernous limestone or a clay formation that is unstable in the extreme. The clay slopes seem almost in motion and are dangerous in the rainy season.

A similar hydrogeological situation is encountered on western part of the island of Java. The springs at Bogor provided a bountiful supply of water to the local people and the port of Jakarta. Now Jakarta has a population of seven million. Less than one-third of the people have water service and many depend on the half-million or more shallow wells. The drawdown from over pumping has reversed the natural hydraulic gradients of this discharge zone, allowing sea- water intrusion and downward flow of contaminants from the surface. As in Kupang, alternative sources for municipal supply are costly and difficult. These centres have simply become too big for the water supply that served them so well in earlier times.

It is really a pretty common thing to see a city that has outgrown its original water source and needs a new one. In most of our experience, this means extensive studies and major capital investment. In Canada, in general, we can buy our way out of this sort of difficulty. In Kupang and Jakarta, it is not easy to see a solution, at any reasonable cost. What is obvious is that the groundwater resource has a high real value and that production must be "maximized" as we say, meaning we must get the most water out of the system that is possible for the longest time and with the lowest possible negative consequences.

We accept the problems and costs of water supplies of cities as one of the consequences of the social dynamism that stimulates their growth. No one is to blame and the answer, for we Westerners at least, is to get more water, whatever the cost. In Canada, at least, we can solve almost any water supply problem by spending money, and this seems to find general favour.

We might like think that in use of water for personal business and profit we would behave more responsibly: we would nuture our resources and think ahead and consider the long-term consequences, with respect both to our own good and that of the common good. The record indicates otherwise.

Consider the man in Nigeria, working his "shadoof" to raise water from the pothole in the dry river bed. At this place no rain has ever been recorded during the three or four driest months. His market garden provides him with a good living. It's not a great step, technically, to dig wells in the alluvium nearby for domestic supply, and then to step out farther and dig wells up to 60 metres deep to reach the water table. Over this region and elsewhere in the "Sahel", groundwater occurs in great abundance in good aquifers. It is not over-exploited, perhaps in part because of local farming tradition and methods, but perhaps also because there is no obvious market for their crops and so no capital is invested in wells and pumps that could quickly deplete the groundwater reservoir. This resource will be available for the use of the next generation at least.

Over- exploitation for agriculture without concern for the needs of future generations is common where the favourable combination of soils, terrain, climate and water are found along with economic opportunity. In the High Plains of the south - central U.S.A. the enormous reserve of groundwater in the Ogallala formation is exploited by some 170 thousand wells for irrigation of crops, that a few years ago were surplus to demands and so supported by Federal subsidies. Regional economy depends on this industry which must be short- lived because of the rapid depletion of the groundwater reserve. The current generation of land-owners are making their living through this depletion. Suggestions for conservation have not been heeded; in fact the owners now get a Tax Depletion Allowance that recognizes their land is depreciating in value as they mine the groundwater.

In the Comarca Lagunera in northern Mexico an extensive irrigated area and the commercial centre of Torreon, with a population of a million or so , depend mainly on groundwater. Here to as in 60 other groundwater basins in Mexico, depletion is a serious matter. The water table has fallen from near surface to 100m and more, and the decline is several metres per year. A regional economy and society is dependent on the resource and in this case there simply is no other resonable alternative, but there is some economic control on over- exploitation - the cost of deepening wells and lifting the water 100 m. Not much scientific study has been done on groundwater in the Lagunera, although it is certain that,here too, the use of the groundwater resource must be maximized. Research or engineering studies are not encouraged by authorities. Perhaps their reluctance is related to fact that some 60% of the adult population suffers symptoms of chronic arsenic poisoning. The groundwater throughout most of the basin exceeds the recommended limit of 0.05 mg/l of arsenic and the political implications are not looked on with much joy by those responsible.

Surface- water developments for export to distant centres is common and now groundwater is viewed for the same purpose. In Libya, an enormous reserve of groundwater was discovered during petroleum exploration in the Sahara Desert. Now, a pipeline some two metres in diameter carries water from the water- well- fields hundreds of kilometers north to Tripoli for irrigation and municipal supply. The reservoir of groundwater is great, but it is also non-renewable. The consequences are irreversible.

A similar plan was made by Mexicans for supplying water to the growing cities of Ensenada and and neighbouring region. Flow in the Colorado River is guaranteed by international treaty but the quality is bad because the water has become salty through evaporation in irrigation in the U.S.A. The aquifers underlying the Sonoran Desert are capable of supplying the Ensenada pipeline but here too, the resource is non-renewable. But the Mexicans have run into another complication. The aquifer is truly regional and extends across the international frontier. Americans have objected to the plan because the drawdown cone will reach into the U.S. one defense is to establish a line of wells on the north side of the border to create a drawdown cone and gradient that will keep their groundwater from flowing south to the Mexican wells. So here we have an international confrontation over groundwater and the spectacle of batteries of wells, not artillery, lined up and ready for a pumping war.

For me, the ultimate in groundwater problems is found in Mexico City, where 20 million people live in a closed basin at 2250 m elevation, using 65m3/s of water of which more than 40m3/s is from groundwater within the basin. The consequences are serious and include land- subsidence, groundwater depletion and contamination, and serious drainage problems. Water demand is increasing at about the same rate as the population, which is expected to be about 30 million by the year 2000. Surface water supplies are almost out- of- the- question. Streams within the basin are too small to be important sources. Streams beyond the basin divides are also too small and where they join with tributaries downstream and have larger flows, they are far below, and far away from the City. The cost of bringing in surface water to the City is more the ten times the cost of producing groundwater from wells: this water has a great marginal value. Groundwater is clearly an important issue in affairs of people in many different times, places, and circumstances. In most cases we can say frankly that groundwater -related problems are not dealt with in a strictly rational manner. In my view, the Technology Transfer Conferences of MOE are good evidence that in Ontario at least, there is a will to do better.

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THE STOUFFVILLE LANDFILL SITE - AN OVERVIEW

I. PROULX AND R. N. FARVOLDEN

Waterloo Centre for Groundwater Research
University of Waterloo
Waterloo, Ontario,
N2L 3G1

Waste Management Incorporated Site #4 (Site 4), also known as the Stouffville Landfill, is located about 40 km northeast of Toronto, on the Oak Ridges moraine. Site 4 was closed in 1985 after receiving some 10 million tonnes of liquid industrial wastes and solid wastes over the course of more than 20 years. Operations at Site 4 were the focus of considerable attention on the part of the mass media for a number of years, owing to the activities of local citizens, who were concerned that their supply of groundwater, and indeed local groundwater resources generally were threatened by contamination from the Site. The net result was that an extensive field studies were done to get evaluate the risk of serious hazard to the environment. In the end, the Site was closed before it had been filled to design capacity.

Site 4 is underlain by Halton Till, a sandy silt till which is draped over the outwash sand and gravel of the Oak Ridges Aquifer.Glacial tills and silty clays of low permeability underlie the Oak Ridges Aquifer. The land surface at the Site has of course been completel modified but originall it was hummocky, with a number of distinct, closed, kettle depressions. The Site is bounded on the north by a broad depression that, in high water stages, drains toward the west, from Musselman Lake, about a km away, to the headwaters of the East Branch of the Holland River; most of the time it is a swampy depression. The Oak Ridges Aquifer is an extensive unit that provides water of excellent quality to municipal, industrial and domestic wells.

Site 4 became a landfill site by accident of opportunity and ownership. It was not chosen because it had what we think of now as the characterisics of a good landfill site. It is interesting to look back now, with the benefit of considerable data, experience at the site, and hindsight, to take advantage of it as a very useful case history.

Waste disposal operations at Site 4 began in about 1962. Both solid- and liquid industrial wastes were dumped. The kettles were used mostly for the liquid because experience showed that the liquids infiltrated quickly so the disposal seemed very effective. The first hydrogeologic studies were done in the late sixties,and shortly after, observation wells were installed for a planned program of monitoring the groundwater levels and water quality WMI assumed ownership and a license to operate the landfill to receive municipal solid wastes, and the application required field tests and reports on the hydrogeology. In 1984, a water sample from a private well adjacent to Site 4 was reported to cause bacterial mutagenicity. MOE responded by mounting a state- of-the- art chemical- and biological study of the groundwater at Site 4.m The final report found no evidence of bacterial mutagenicity.

When WMI applied to have the license for Site 4 renewed, it was clear from the opposition of representatives of local citizens groups, and some others, that the landfill was still seen as a threat to the well- being of the local communities. Agreement was finally reached between the owner (WMI), MOE, and the Town of Stouffville for a hydrogeologic study of the Site followed by closure of the Site in 1985. The results of the hydrogeolgic study were submitted to MOE in 1985, by Conestoga Rovers Associates, consultants for the owner.

Since 1970, some 170 observation wells and leachate wells have been installed at Site 4, of which 79 were completed in the Oak Ridges Aquifer and 17 penetrate the entire aquifer thickness. Geophysical logs, including electrical logs, natural gamma logs and caliper logs were made for these 17 holes.

A plume of contaminated groundwater has been identified and is moving toward the southwest from the Site. Chloride is the best parameter for identifying and describing the plume. Changes in ratios of other parameters to the chloride ion are useful in determining chemical processes in the plume. Tritium data suggest that the oldest part of the plume was water that was "dead" with respect to tritium when is was disposed of in the lagoons some 25 years ago. The industrial liquid wastes disposed of at Site 4 were from industries in the Toronto region that use municipal water from Lake Ontario, which is "dead" with respect to tritium. Even within the plume of contminated groundwater, the water quality meets most, or all, MOE standards for drinking water.

Some uncertainty remains as to whether or not leachate from the solid waste in the Halton Till has migrated downward and reached the aquifer. The chloride plume (and plumes for other parameters) is weaker under the centre of the landfill than donwgradient in core of the plume. This can be interpreted as a plume that has a source that has weakened or disappeared. Samples from the top of the saturated zone, in the Oak Riges Aquifer, under the landfill, have very low concentrations of any contaminants.

Estimates of the migration velocity of a plume at Site 4 have varied over a wide range. Field monitoring and modeling give a velocity of 35 m/year.

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COMPARISON OF EXPERIMENTAL MUNICIPAL REFUSE COLUMN STUDIES WITH LANDFILL FIELD TEST CELLS

D.W.KIRK AND S.PIRANI
DEPARTMENT OF CHEMICAL ENGINEERING AND APPLIED CHEMISTRY
UNIVERSITY OF TORONTO

Key words: Municipal Refuse, Leachate Modelling, Scale-up

INTRODUCTION

The determination of the impact of municipal refuse disposal on the environment is a very important but complex issue. The use of landfill disposal will continue to be the most accepted means of disposing of municipal refuse. The generation of leachate from these landfill sites will have an impact on the surrounding ground water. Capping the refuse site can reduce the infiltration of moisture and can limit the quantity of leachate generated. However the complete sealing of moisture input and output is neither practicable nor desirable. Therefore to shed light on the mechanisms of leachate generation and composition and to determine the effects of hazardous materials codisposed with municipal refuse, there is a need to conduct basic experimental research. Unfortunately, conducting research in a municipal refuse site is exceedingly difficult and the results are difficult to interpret.

One approach to conducting municipal refuse research has been to use laboratory scale leaching columns packed with municipal refuse. Although the experimentation is relatively easy to perform, the effects of some of the complex interactions found in the field are lost. Large objects (usually metal) must be excluded due to the column size, the municipal refuse must be homogenized, the microbial population growth is seldom established, and the leachate hydrodynamics are not developed in the same way as in the field. As a result, there is difficulty in relating laboratory results to field situations. At present there is no direct means of interpreting laboratory data and actual field behaviour. This difficulty of using laboratory scale leach tests to predict field behaviour raises concerns about the applicability of the Leachate Toxicity Test used to classify the hazardous nature of solid wastes. Clearly, a means of conducting laboratory scale experiments so that field behaviour could be predicted, would be very valuable.

The work presented in this paper represents part of the on-going research into the effects of co-disposal of industrial and municipal wastes. The focus of this paper is on the question of relevance of column study leachate results using municipal refuse to field studies of municipal refuse leachate. The columns used for this study have been in continuous operation for over 1000 days and various aspects of this work have been previously reported [1]. The columns, although relatively large for laboratory scale are small compared with field test cells and present significant advantages over field test cells. The difficulties associated with field test cells are manifest by the few reported experiments in which water throughputs have been measured. The column studies presented in this paper are compared with field study data performed for the U.S. EPA at three different sites in the U.S.A.. These EPA studies provide a limited number of parameters for comparison but can be divided into both small and large field experiments for exploring size effects in municipal refuse test cells. Variability of parameters due to uncontrolled factors such as heterogeneity and environmental conditions require that some data averaging be performed. The techniques for data normalization and averaging are discussed.

EXPERIMENTAL

COLUMN STUDY

The column study[1], supported by the Ontario Ministry of the Environment was designed to simulate field conditions and to investigate the effect of co-disposal of a hazardous solid waste on the municipal refuse environment. There are 16 columns in operation packed with 4 different compositions: 100% municipal solid waste(MSW), MSW + 8% industrial waste(IW), MSW + 30% IW and 8% IW in sand. The high density polyethylene cylindrical columns are 1.93m high, and 0.33m in diameter and contain approximately 43 kg (dry weight) of MSW. One half of the columns receive moisture input from precipitation while the other half receive controlled periodic water additions. The systems are maintained in unsaturated flow conditions with regular leachate removal from the bottom reservoir. Three MSW columns, column number 1,2 and 3, are used in the comparison with small and large field cells. This study is on-going amd the columns have been in continuous operation for over three years.

SMALL FIELD CELLS

The data from two different U.S. EPA small field cell studies are used to compare with the column study.

The Boone county study[2] located in Kentucky, U.S.A., was established to investigate production of leachate from MSW field cells and other environmental effects on leachate generation. Five sanitary landfill cells, one large, one medium and three small field cells, were constructed. Two small field cells, BCFS #2A and BCFS #2B were used in the comparison for this paper. The cells were enclosed in cylindrical steel pipes, 1.83m in diameter and 3.66m high and contained approximately 2,100 kg (dry weight) of municipal refuse. The cells were constructed in August 1972, and the research concluded with the site closure in August 1980.

The Center Hill study[3] located in Cincinnati, Ohio, was established to investigate solid waste decomposition and contaminant release in various types of simulated landfills including the effects of codisposal with industrial wastes. A total of 19 small field cells were constructed in late 1974 and early 1975. Each test cell contained approximately 1,800 kg (dry weight) of municipal refuse. The cell size was identical to the one used in the Boone county study. The C.Hill #4 cell containing MSW only and receiving 813 mm/year of water, was selected for the comparison in this paper. The operation was terminated and cells were disassembled in April 1983.

LARGE FIELD CELLS

The data from two different U.S. EPA large field cell studies are used in the comparison for this paper.

The large field cell data from the Boone county study described above was used. The dimensions of the cell BCFS #1 were 45.4m x 9.2m and contained approximately 286,000 kg (dry weight) of MSW.

The Sonoma County, California[4] study investigated the effect on refuse stabilization of applying excess water, septic tank pumpings and recirculated leachate. A total of five field cells were constructed and monitored for over four years, from late 1971 to early 1976. The test cell Sonoma C used in the comparison for this paper was a control cell approximately 18 meters square by 3m deep. This cell contained approximately 352,000 kg (dry weight) of MSW and was operated similarly to BCFS #1 cell.

CELL DATA

Summarized data for the test cells is presented in Table 1.

TABLE 1. SUMMARY OF TEST CELL DATA

Test cell	Avg. Annual Leachate (l/kg/year)	Refuse Mass Dry Weight (kg)	Max. Refuse Depth (m)	Refuse Dry Density (kg/m3)
FIELD				
BCFS #1	0.57	286,000	2.56	429
SONOMA C	1.91	352,000	2.62	460
SMALL				
BCFS #2A	0.60	2,046	2.56	304
BCFS #2B	0.58	2,113	2.56	314
C. HILL #4	0.99	1,855	2.4	290
COLUMN				
COL #1	1.21	42.9	1.8	299
COL #2	1.21	43.1	1.8	300
COL #3	1.91	42.8	1.8	298

-BCFS #2A,#2B, BCFS #1 .... ref.2
-C.HILL #4 .... ref.3
-SONOMA C ref.4
-COL #1,#2,#3 ....this work

The average annual leachate production per kilogram of dry refuse for the column study varies from 1.22 l/kg for environmental precipitation to 1.91 l/kg for controlled water addition, and is greater than for the small test cells and BCFS #1 field cell,but is smaller than for the Sonoma C field cell. The refuse mass is 47 times smaller than small cells and is approximately 7,400 times smaller than the large field cells. The refuse depth is approximately 1.4 times lower than both small and large field test cells. The packed refuse dry densities for the columns and small field cells were very similar, however, densities were approximately 1.5 times smaller than the large field cells.

COMPARISON PARAMETERS

Many parameters were monitored in the various studies compared, however, only 9 parameters listed in Table 2. were common to most studies.

TABLE 2. LEACHATE PARAMETERS COMPARED

Parameter	BCFS #1	SONOMA C	BCFS #2A, 2B	C. HILL #4	COLUMNS #1, #2, #3
pH	x	-	x	x	x
COD	x	x	x	x	x
Calcium	x	x	x	-	x
Zinc	x	x	x	x	x
Iron	x	x	x	x	x
Manganese	x	-	x	-	x
Magnesium	x	-	x	-	x
Sodium	x	x	x	-	x
Potassium	x	x	x	-	x
Chloride	x	x	x	x	x

RESULTS AND DISCUSSION

Graphical Comparison

The average concentration history and mass removal curves comparing leachate form the column study to both small and large field test cells are presented in Figures 1-11. The concentration or cumulative mass removal has been plotted against cumulative leachate volume rather than time since the leachate concentration trends and subsequent mass removals are more leachate volume related. Leachate volume and mass removal data are also normalized by dividing by the dry weight of the refuse to account for the different sizes of the cells.

The sampling intervals and leachate flow rates for all studies were different and were therefore, normalized by calculating weighted mean concentrations of the leachate parameters at common points in the leachate flow history. This was done by calculating the mass of the parameter (concentration times water volume) that was removed from the refuse between sample analyses over the interval of leachate flow, usually 0.5 l/kg of dry refuse. This mass was then divided by the volume of leachate to give a weighted mean concentration for the leachate volume interval. Cumulative mass removals were obtained by adding the incremental masses used in calculating the weighted mean concentrations.

pH

The variation of pH is shown as a function of leachate volume in Figure 1. The upper and lower lines drawn in the figure are the +/- 1 standard deviation values of the mean pH values of the leachate for the column and small test cell experiments. There is clearly a significant variation of pH within these studies. Only one of the large field test cells had reported pH values and the variability of these data were as great as in the smaller scale studies.

COD

The variation of COD as a function of leachate volume is shown in Figure 2. The upper and lower lines drawn in the figure are the +/- 1 standard deviation values of the weighted mean concentrations for the column and small test cell experiments. The upper and lower values for the large test cells are the upper and lower weighted mean concentrations for the two large scale experiments. For the COD data there is a clear trend of higher initial values for smaller scale experiments. This distinction is lost after 2 l/kg leachate have been generated.

The initial difference between the small and large scale experiments is also reflected by the total mass removal of COD as shown in Figure 3. The column and small field cells appear to be able to release significantly more COD per mass of refuse than the large field cells. However, this difference is primarily due to the initial concentration differences in the first 1 to 2 l/kg of leachate produced.

Zn,Mn

The variation of concentration of Zn and Mn as a function of leachate volume is shown in Figures 4 and 5 respectively.For these elements, the trend is for the larger scale experiments to show higher initial values. After approximately 1 l/kg leachate has been generated the concentration profiles overlap.

Ca,Cl,Mg,K,Na

The variation of concentration of Ca,Cl,Mg,K,and Na as a function leachate volume is shown in Figures 6,7,8,9 and 10 respectively. These elements have been grouped because there is a trend for the initial concentrations to be higher for the smaller scale experiments. After approximately 1 to 2 l/kg of leachate has been generated the concentration profiles overlap.

Fe

The variation of concentration of Fe as a function of leachate volume is shown in Figure 11. The iron concentration history is unlike that of other elements because of the relative constant concentration after the initial 1 l/kg of leachate. The three different experimental scales show remarkably similar concentration histories.

From the concentration profiles of the elements studied there appears to be a greater tendency overall for the smaller scale experiments to show higher initial concentrations. This behaviour might be associated with the packing density or shredding carried out in the small scale studies. There is better agreement between the small field cells and the column studies, which have similar packing conditions, than with the large field cells. This association with packing density is tenuous since not all elements are similarly affected. Indeed the similarities of the leachate concentrations from all the experimental measurements are more striking than are the differences.The leaching behaviour was modelled with first order kinetics for each of the elements.

$$C(V) = C^{o}\exp(kV)$$

The concentrations modelled were the weighted mean concentrations and the time function used was the normalized leachate volume l/kg (see Table 3). The C^{o} value is the least squares fitted concentration at 0 leachate. Average regression correlation coefficients, r, of greater than 0.99 were found for the column studies, greater than 0.97 for the small field test cells, and greater than 0.94 for the large field test cells. The exception for all the studies was the iron behaviour. The iron concentration is clearly not first order with time or leachate volume, nor do the concentrations vary with pH change as has been suggested in the literature. The source of the constant iron concentration is most likely the ferrous waste in the municipal refuse but the leaching mechanism is not yet established. The only other element to have a weak correlation coefficient with first order kinetics was chloride in the large field test cells. The poor correlation was the result of an apparent increase in chloride concentration with time in the one of the large field cells (Sonoma C).

The similarities in leaching behaviour for the three experimental scales, included the degree of data fit to first order kinetics and the concentration values of all the species studied after the initial period of 1.5 to 2 l/kg of leachate. Even the iron concentration profiles which do not conform to the kinetic model are very similar for the three experimental sizes The concentration normalization used did not eliminate the generally higher initial concentrations found in the smaller scale experiments. The values of the parameters used to fit the first order kinetics shown in Table 3 demonstrate the variability between the three experimental scales.

TABLE 3. EQUATION CONSTANTS FOR $C=C^0EXP(kV)$

PARAMETER	COLUMN STUDY			SMALL CELLS			LARGE CELLS		
	C^0	RATE	r	C^0	RATE	r	C^0	RATE	r
COD	89	-.77	.982	57	-.46	.983	38	-.52	.992
CALCIUM	5.1	-.73	.991	2.25	-.47	.987	1.65	-.43	.976
ZINC	0.11	-.83	.984	0.16	-.97	.971	0.13	-1.45	.909
IRON	0.67	-.08	.311	0.63	-.05	.316	0.54	-.21	.699
SODIUM	3.83	-1.12	.992	1.57	-.94	.979	1.05	-.59	.994
POTASSIUM	2.59	-1.19	.983	2.19	-.95	.993	0.89	-.58	.987
CHLORIDE	5.06	-1.43	.989	1.39	-.82	.926	0.93	-.30	.704
MANGANESE	0.09	-.73	.985	0.05	-.54	.949	0.11	-.75	.989
MAGNESIUM	0.77	-.92	.988	0.49	-.73	1.0	0.41	-.66	.987

C^0 fitted initial weighted mean concentration g/l
RATE rate constant k
V cumulative leachate volume l/kg dry refuse
r regression correlation coefficient

CONCLUSIONS

1 A first order rate equation is suitable for modelling concentration profiles in leachate from column studies to large scale field studies of municipal refuse. The exception, found from the elements studied, was iron. The significant amount of iron waste in municipal refuse leads to a relatively constant concentration over the period studied.

2 The normalization of the time scale through the use of the leachate volume produced per mass of refuse, and the use of weighted mean concentrations are very effective in comparing data from different studies and scales of studies.

3 After the first 1 to 2 l/kg of leachate, the modelled column data could be used to predict field behaviour to a least 4.5 l/kg of leachate. The extent of the model validity will be further assessed as the study progresses.

4 An increase in the scale of the study of municipal refuse leachate generation does not directly lead to increases or decreases in leachate contaminants though for the limited number of elements that were available for comparison more were found to be less concentrated with the larger scale experiments.

5 The column studies used in this work appear to provide a very good means for relating the effects of codisposal parameters to field behaviour.

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ACKNOWLEDGEMENTS

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FIG. 1 LEACHATE PH

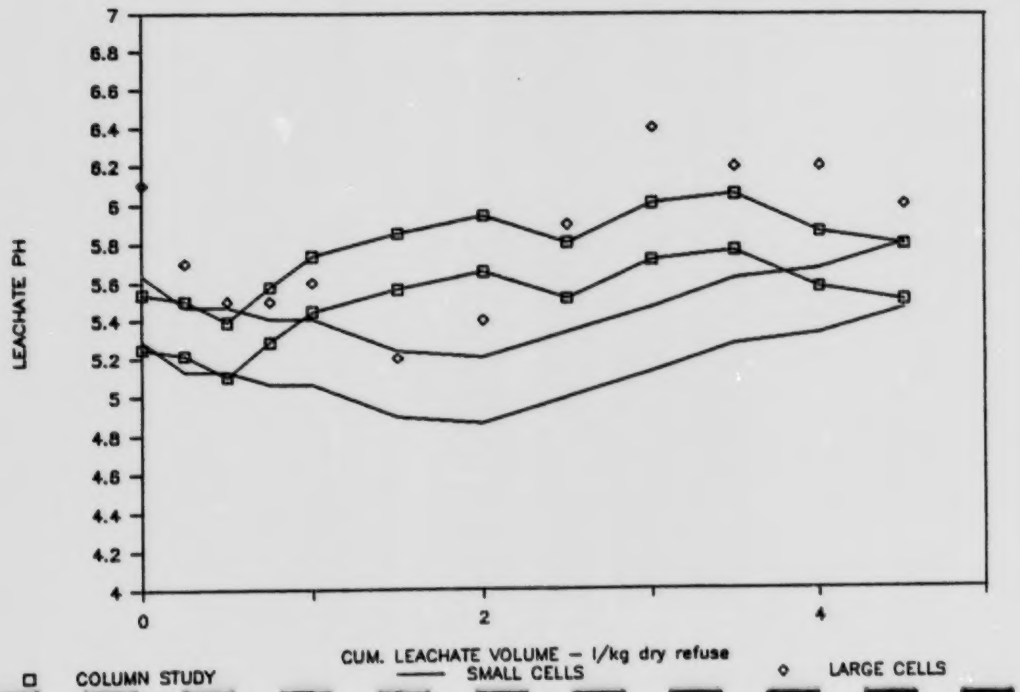


FIG. 2 COD CONCENTRATION HISTORY

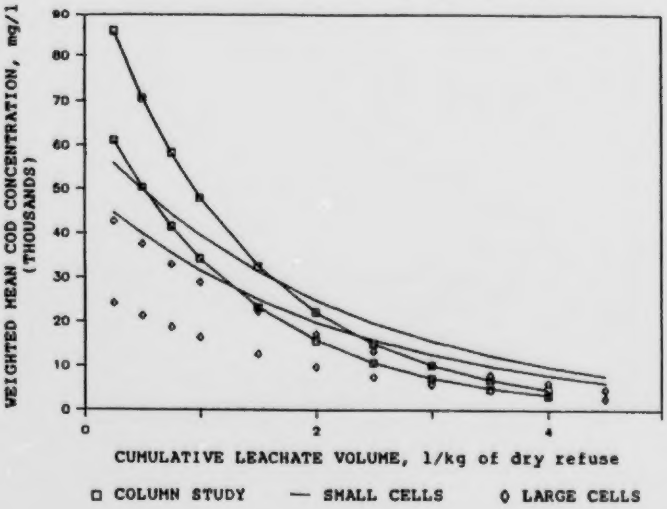


FIG. 3 COD MASS REMOVAL

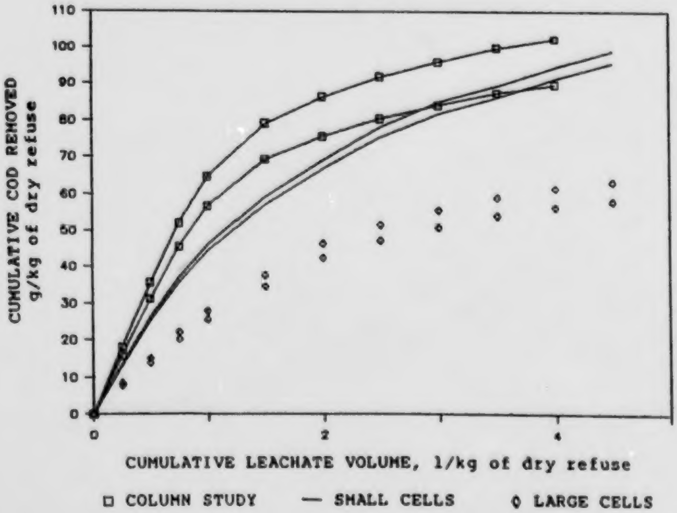


FIG. 4 ZINC CONCENTRATION HISTORY

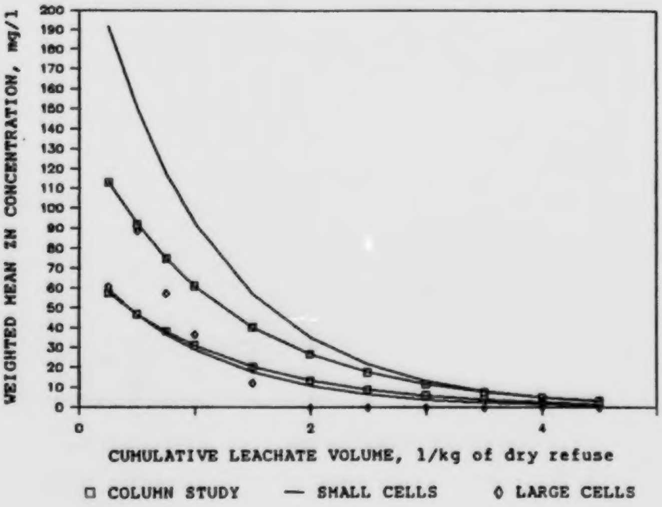


FIG. 5 MANGANESE CONCENTRATION HISTORY

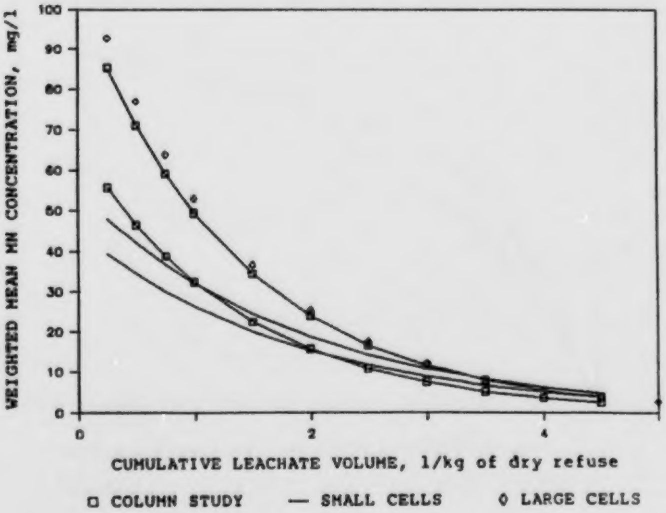


FIG. 6 CALCIUM CONCENTRATION HISTORY

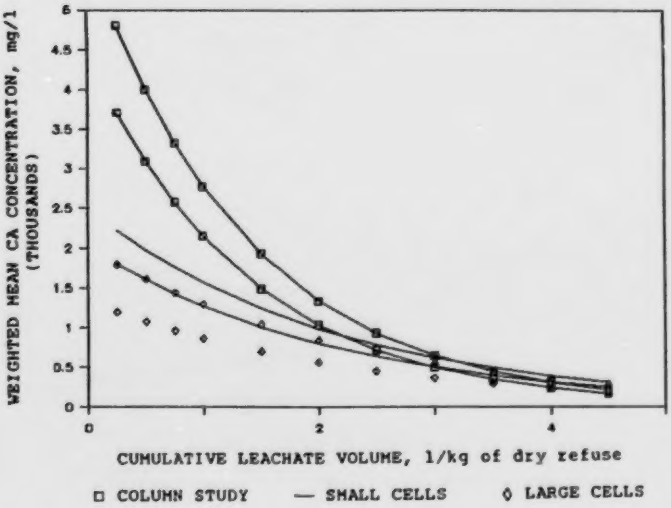


FIG. 7 CHLORIDE CONCENTRATION HISTORY

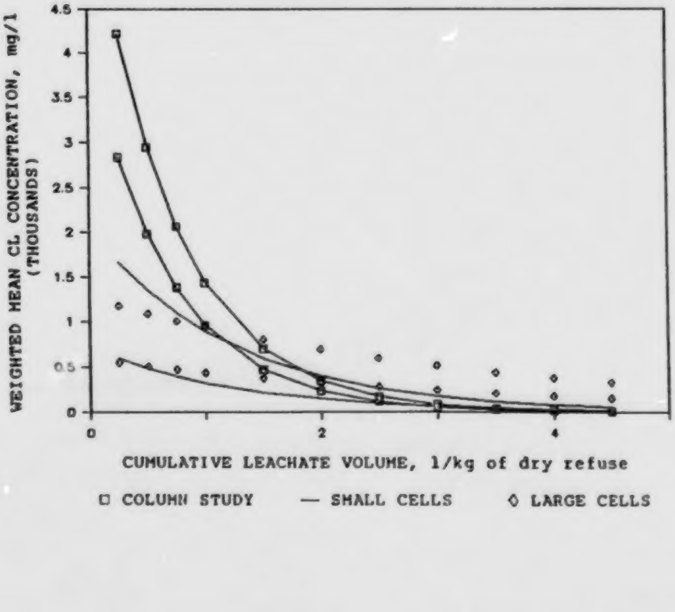


FIG. 8 MAGNESIUM CONCENTRATION HISTORY

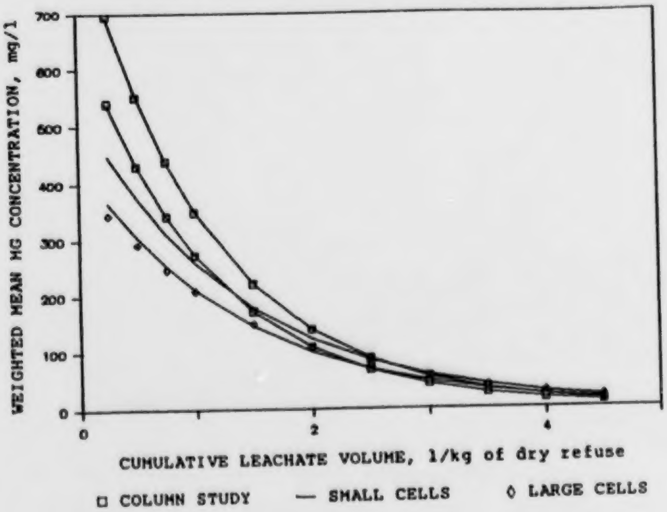


FIG. 9 POTASSIUM CONCENTRATION HISTORY

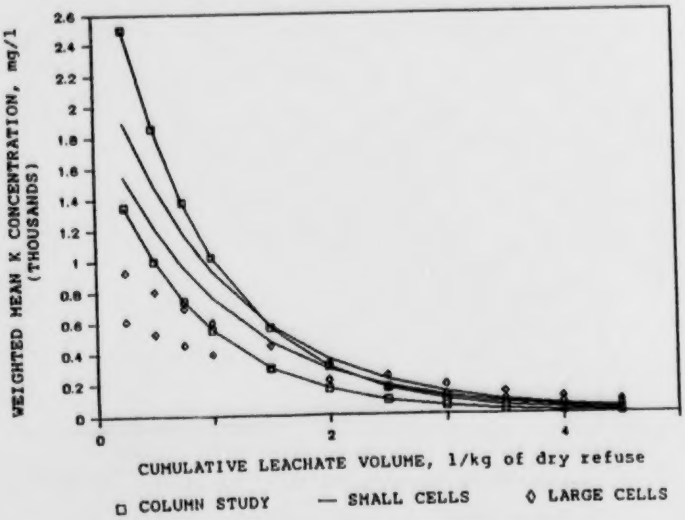


FIG. 10 SODIUM CONCENTRATION HISTORY

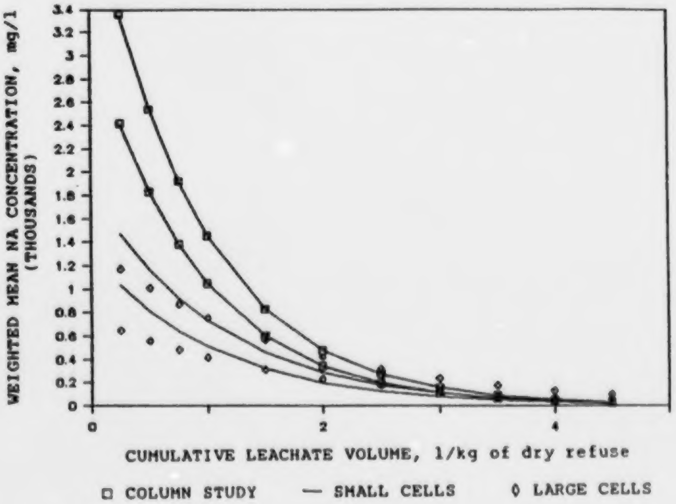
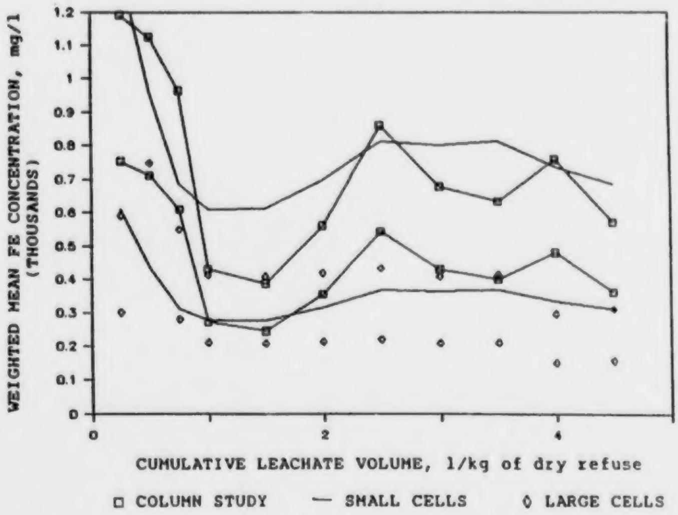


FIG. 11 IRON CONCENTRATION HISTORY



C15

THE ALTERNATIVE TO INCINERATION OF BIOMEDICAL WASTE
- HAMMERMILL/CHEMICAL DECONTAMINATION

by

John Manuel,P.Eng. and Paul A.W.Gamble
Senior Consultant
M.M.Dillon Limited
Toronto M2N 6H5

Paul A.W.Gamble
Associate Executive Director
Hospital Council of MetroToronto
Toronto M5B 1J3

The Hospital Council of Metropolitan Toronto (HCMT), a voluntary hospital association representing the hospitals in and around Metropolitan Toronto, has requested approval from the Ontario Ministry of the Environment (MOE) to demonstrate the suitability of an alternative technology for the processing of biomedical (hospital) waste. This technology is known as shredding/disinfection and, in the United States, has been shown to reduce the volume of, and render innocuous, biomedical wastes from hospitals.

At the present time, on-site incineration is the primary method of disposing of biomedical waste generated at Toronto hospitals. Because of concerns about emissions from most incinerators, an alternative environmentally suitable and cost effective technology has been sought by HCMT on behalf of its fifty-two member hospitals.

HCMT proposes to build a two million dollar technology demonstration facility at the site of the existing Booth Avenue Hospital Laundry plant at 40 Booth Avenue, in the City of Toronto. The laundry plant is a non profit shared service organisation owned and operated by thirteen Toronto hospitals. The demonstration work will take about six months to complete, beginning in Mid 1989. Test quantities of hospital (yellow bag) waste, in sealed containers, will be transported in MOE approved refrigerated trucks from participating hospitals (members of HCMT) to the Booth Avenue facility for processing.

A number of studies, such as microbiological evaluation as well as chemical and physical testing will be carried out during the demonstration period to assess the efficacy of the alternative treatment. After the equipment is in place, but before it is put into service, air samples will be collected from the workplace and outside the building and analysed for ambient air conditions and micro organisms that can be transmitted to humans via the airborne route. These procedures will be repeated after the equipment is put into operation.

Before infectious (yellow bag) waste is processed, bags of simulated waste will be seeded with known concentrations of indicator organisms. Half of these bags will be treated with 12% sodium hypochlorite and, as a control,the other half will be treated with normal tap water. The efficiency of disinfection by chlorine can often be improved by pH alteration; therefore, variations in the pH will be investigated in both the simulation and operational phases. The proposed micro organisms test protocol range is shown in Appendix 1.

Following the demonstration period, a report on the accumulated experience and findings of an expert review committee will be subjected to the Environmental Assessment process prior to a final decision being made with respect to the establishment of a permanent location for a biomedical waste shredding/disinfection facility.

The processing technology consists of a slow-speed shear shredder followed by a high-speed hammermill. The shredded material is disinfected at the same time by saturating it with a solution of sodium hypochlorite. (This solution is also known as commercial bleach).

The entire shredding/disinfection process is enclosed so it can be maintained under negative pressure, meaning that there can be no escape of waste material or fumes to the building interior. The air exhausted from the equipment enclosure is passed through special high-efficiency filters before being vented through a duct above the building roof. (See attached illustration).

Shredded disinfected residue will be retained within the site until there is confirmation of micro-organism kills efficacy. The waste treatment process generates a wastewater stream containing residual hypochlorite solution and very fine particulate material (mainly glass). After this waste stream is monitored, it is combined with the wastewater from the existing hospital laundry plant and safely discharged to the City of Toronto sewer system. The laundry presently adds hypochlorite solutions to the laundry wastewater in order to render the wastewater acceptable for discharge to the sanitary sewer system.

To ensure proper and thorough review of the results of the experimental work, a team of highly qualified technical specialists has been assembled. Under the chairmanship of Dr. Patricia Seyfried of the University of Toronto's Department of Medical Biology, the team consists of representatives of:

- The City of Toronto Department of Public Health
- The Ministry of Health
- The Ministry of the Environment
- The Hospital Council of Metropolitan Toronto

The technology will be assessed using a detailed protocol addressing all aspects of safety, microbiology, chemistry, operating procedures as well as the acceptability to current applicable legislation and regulations.

APPENDIX 1

PROPOSED PROTOCOL FOR TESTING OF MICRO ORGANISMS

Viruses:

Enterovirus (polio vaccine strain)
Adenovirus (enteric strain)
and/or RNA phage
Coliphage

Bacteria: Total heterotrophs
Fecal coliforms
Escherichia coli
Pseudomonas aeruginosa
Salmonella sp.
Klebsiella pneumoniae
Mycobacteria
Mycoplasma
Clostridium perfringens
Clostridium difficile
BAcillus cereus

Parasites: living Acanthamoeba and Naegleria; Giardia and Cryptosporidium cysts

Fungi: Total fungi

Endotoxins

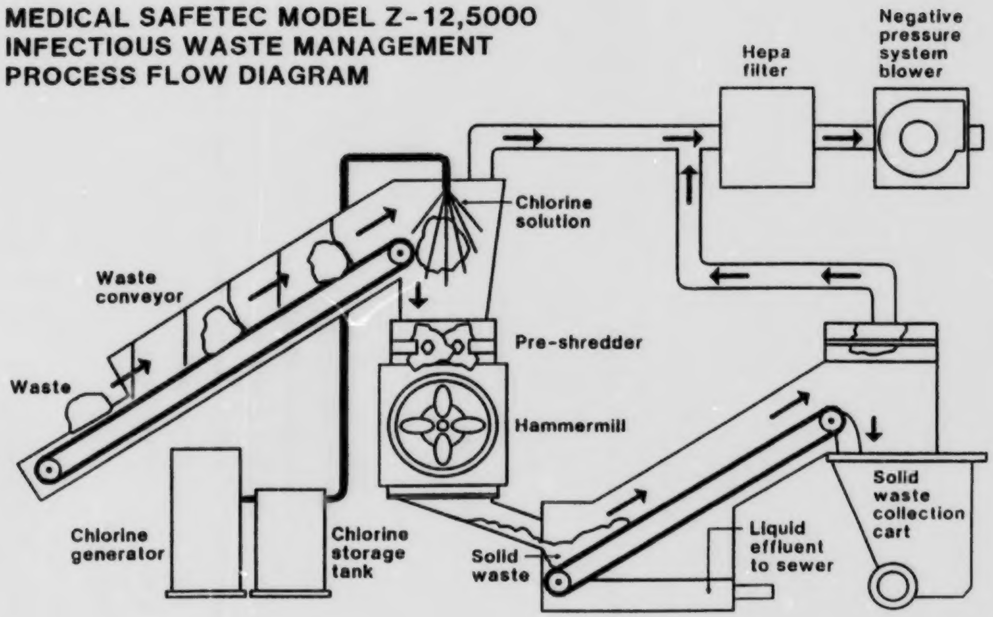

MEDICAL SAFETEC MODEL Z-12,5000
INFECTIOUS WASTE MANAGEMENT
PROCESS FLOW DIAGRAM
Hepa filter
Negative pressure system blower
Chlorine solution
Waste conveyor
Pre-shredder
Waste
Hammermill
Solid waste collection cart
Chlorine generator
Chlorine storage tank
Solid waste
Liquid effluent to sewer

FIGURE 1. PROPOSED TREATMENT OF BIOMEDICAL WASTE (HCHT)

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EROSION OF LANDFILL COVERS

J.H. Cuthill
Department of Land Resource Science
University of Guelph
Guelph, Ontario

Kevin J. McKague, P.Eng.
Agricultural Engineer
Ecologistics Limited
Waterloo, Ontario

Dr. W.J. Stolte, P.Eng.
Department of Civil Engineering
University of Saskatchewan
Saskatoon, Saskatchewan

1.0 INTRODUCTION

With many landfills in Ontario having reached their capacity and thus been decommissioned, questions are being raised as to the long-term stability of landfill caps. How susceptible are covers to erosion and gullying? What cover management and maintenance is required? Do present landfill caps maintain the fine balance between minimizing infiltration and leachate production while at the same time avoiding the loss of liner integrity as a consequence of erosion? Little research on this topic has been completed in Ontario to date. Upon analysis of the data and observations made in this yet to be completed one-year study, answers to the above questions can begin to be formulated, providing direction for possible further research in this area in future years.

2.0 LITERATURE REVIEW OF EROSION AND ITS CONTROL ON LANDFILL COVERS

To begin to understand water erosion as it relates to landfill caps, a review of literature covering the topic was conducted. One American study in the State of Pennsylvania reported that of 24 Pennsylvania landfills inspected, 33% showed only slight erosion problems, 40 % had moderate erosion problems, while nearly 20% had severe erosion problems. Personal observations made by Johnson (1986) in the Great Lake States area agree with these Pennsylvania findings.

Landfill covers perform a number of functions. Lutton et al. (1979) included in their list the following:

Prevention or Minimization of Percolation
Promotion of Aesthetics
Suppression of Vectors
Containment of Gases
Suppression of Fire Danger
Prevention of Blowing Litter or Dust
Promotion of Site Reclamation

To perform these functions for the life of the landfill a good cover must possess the following attributes (Lutton et al. 1979):

Resistance to Water Erosion
Resistance to Wind Erosion
Stability Against Slumping and Cracking
Stability Against Slope Failures
Resistance to Cold-Weather Distress
Resistance to Disruption by Animals or Plants

Documents which provide insight into designing a landfill cover to achieve the desired cap functions noted the dilemma designers are faced with when choosing measures to minimize water erosion of the cap. A good vegetative cover is the most economical and practical technique available in preventing soil erosion because it slows the surface water velocity and encourages water to infiltrate the soil. Unfortunately, the increase in infiltration capacity ultimately leads to a higher rate of leachate production. The cost of treating the additional leachate can become quite significant in itself. Despite this dilemma, it was the conclusion of most reports that establishment of durable vegetation is the most effective method of erosion control. In instances where infiltration rates are to be kept low, especially on more hazardous waste sites or where leachate production is to be minimized, synthetic caps and or drainage collection systems combined with structural surface water control measures such as diversion terraces, waterways and rock chutes may need to be implemented. Most of the techniques that have been applied to control erosion on landfills are methods that have been used successfully in the past to combat erosion on agricultural land and in road construction.

Additional factors need to be considered when establishing a vegetative cover on a sanitary landfill site than are normally considered in agricultural erosion control work. Not only do plant species need to be selected for their ability to withstand the nutrient and pH conditions in the cover soil, they also need to show signs of tolerance to the presence of gases in the root zone. Droughtiness is also a problem given the fact that in most cases the cover top soil (if any exists) used to support vegetative growth is quite thin. Johnson (1986) recommends a minimum of 0.6 m (2′) of plant growth medium to maintain adequate moisture levels to support vegetation under drought conditions.

Plant species recommended in the literature in general included shallow-rooted plants with high transpiration characteristics. The ideal plant cover was described as being one that would protect the surface against raindrop impact, bind soil in the zone with a dense, fibrous root system, not penetrate the clay cap and be immune to the invasion of shrubs and trees. Johnson (1986) described quackgrass as having many of the desired erosion control characteristics although it is classed as a noxious weed among agricultural personnel. Site specific test plots were generally regarded as being necessary to determine which species would ultimately establish themselves well on individual landfill sites.

When applying the seed it is recommended it be planted on the contour if possible. Mulch should accompany the seed. Lutton (1987) suggests that almost any material may be used as a mulch to provide surface and seed protection until adequate vegetation has been established. Straw mulch is most economical and is best applied at a rate of 1.5 tonnes/ha where erosion is not anticipated, and 2.0 tonnes/has where erosion threatens. Petroleum based mulches are effective as a mulch at an application level of 9,400 to 11,400 litres/ha. Erosion fabrics may need to be utilized in some instances to stabilize the soil surface during its critical vegetative establishment stage.

While protecting a landfill cap from the elements with vegetation is one means of reducing the impact of water erosion on cap integrity, limiting slope lengths and gradients associated with the cap is another means of reducing erosion potential. One US-EPA publication recommends slopes of a landfill site be graded to at least 5% but no greater than 18% in order to promote runoff without excessive erosion. This is to balance efficient shedding of runoff water with consideration for water erosion hazards.

Directing surface water flow by means of the various water control structures outlined previously can safely remove runoff water from the cap's surface if vegetative protection alone is not sufficient.

The US-EPA has suggested using the Universal Soil Loss Equation (USLE) as a tool to evaluate the surface layer configuration of landfill covers. They also suggest a tolerable soil loss of 4.5 tonnes/ha/year (2 tons/acre/year) be achieved when designing landfill cover erosion control systems. Luther (1980) also suggests the USLE be used to approximate the erosion losses from a landfill cap.

3.0 SURVEY OF LANDFILL COVER EROSION IN ONTARIO

3.1 Objective

The objective of this component of the present study is to determine whether soil erosion associated with municipal landfill sites, as they are presently designed, constitutes a problem with respect to the long-term stability of landfill covers in Ontario.

3.2 Method

The investigation to determine the existence or extent of erosion problems on landfill sites in Southern Ontario was conducted first by contacting all three Southern Ontario Regional Offices of the Ministry of the Environment to obtain names of and information on waste disposal sites suitable for the study (i.e. decommissioned, or at least part of the site decommissioned, and having received its final vegetative cover). This provided the study team with approximately ten sites to visit. Other sites, besides those provided, which were known to exist by the study team were also visited following receipt of approval to enter the site by the operator.

Site visits were a time both to qualitatively assess the site with respect to erosion as well as collect data necessary to quantitatively estimate average erosion rates. At the time of writing 14 sites were visited and the results assessed. Sites to which visits were made were kept confidential.

3.3 Qualitative Results From Site Visits

Soil erosion can be relatively easy to detect when it has progressed to the point where gullies are being formed. In fact, it is normally the development of large gullies that prompt remedial measures be undertaken to control the erosion long before the more subtle interrill and rill erosion spurs action.

For the 14 sites visited, a wide variety of conditions were encountered with respect to landfill cover soil types, vegetative cover, size of landfill and age of landfill. While it is difficult to generalize, it would appear that the amount of vegetative cover had more influence on the severity of erosion than did the landfill cap's soil type. Figures 3.3.1 and 3.3.2 give an

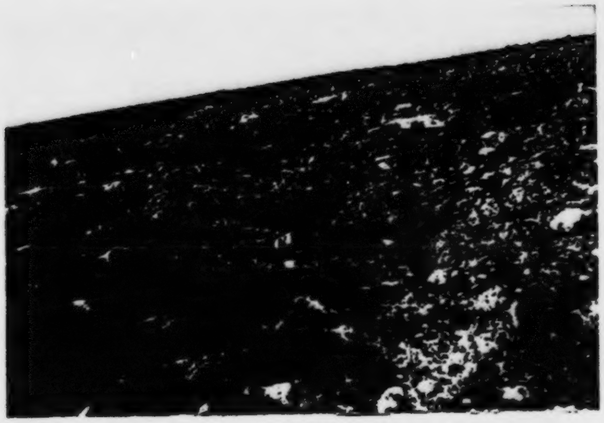


Figure 3.3.1: Severe Interrill & Rill Erosion on a Landfill Cap

Figure 3.3.2: Landfill Cap with a Well Established Natural Cover

indication of the range in vegetative cover encountered; everything from essentially bare soil conditions to covers supporting trees and natural vegetation. South facing slopes appeared to have the greatest difficulty growing and maintaining vegetative covers.

Gully erosion was present at all but three sites. For the better vegetated and often older sites, the gullies appeared to have been created in previous years and were now slowing in development. For the larger landfill sites possessing long steep slopes, seepage resulting from subsurface lateral flow between soil layers along with preferential flow paths caused by compaction by equipment used to place the cover became the more dominant causes of gully formation. For other landfills having flatter tops, areas where surface water concentrated to flow over the steep edge would often give rise to gully development at that point. Figure 3.3.3 illustrates such a situation.

For landfills at which maintenance personnel were still available, the large gully problems were normally dealt with quickly by placing rock or fill in the gullies.

3.4 Quantitative Estimates of Erosion at Sites Visited

At each site visited data was collected which would be useful in estimating typical erosion rates of the landfill cap through the application of the Universal Soil Loss Equation (USLE). The USLE is an empirical relationship that has been used extensively by soil conservationists in agriculture to estimate field interrill and rill erosion rates on agricultural land and has been used in the past in the United States as a means of estimating the susceptibility of landfill covers to erosion. Table 3.4.1 summarizes the results from this analysis.

Note that the USLE erosion estimates do not include those losses associated with gully erosion. This form of erosion was found at nearly all the landfill sites visited. Consequently the USLE will underestimate the total soil loss being experienced on the landfill sites visited for it does not consider all of the soil loss mechanisms associated with a landfill cover. At present however, it is the best means available for quantifying rill and interrill soil losses. Values in Table 3.4.1 were based on the typical slope lengths and gradients and vegetative cover found on the site. Slope lengths and gradients are self explanatory. Vegetative cover was categorized in the following manner:

Poor - Up to 30% of canopy cover and/or up to 30% ground cover

Fair - 30% to 70% canopy cover and/or 30% to 70% ground cover

Good - Greater than 70% canopy cover and/or more than 70% ground cover

Based on these results, nearly 30% of the sites visited have interrill and rill erosion losses in excess of the tolerable level of 4.5 tonnes/ha/year. Figure 3.4.1 taken at one site where the erosion rate exceeds the tolerable level graphically illustrates the consequence of such loss rates on a landfill cap and its surrounding area.

Table 3.4.1: Interrill and Rill Erosion Estimates for Visited Landfills

Site Number*	Estimated Typical Erosion Rate (Interrill & Rill Erosion only) (Tonnes/ha/yr)	Typical Slopes**]		Vegetation Condition
		Length (m)	Gradient (%)	
1	4.5	15-40	2-12	Fair
2	0.23	50	14	Fair to Good
3	1.0	10-40	2-16	Good
4	0.1	10-100	2-9	Good
5	10.40	45	11	Fair to Good
6	0.92	10-44	15-18	Good
7	41	25-75	2.5-20	Fair
8	23	20-30	2.2-15	Poor
9	1.62	5	12	Fair
10	1.15	5-35	2-3	Poor
11	20.3	15-45 (one slope as long as 320 m)	2.75-15	Poor
12	1.15	15	40	Fair
13	2.7	10-25	1-30	Fair to Good
14	3.03	30	12	Good

* Sites were located within the jurisdiction of the southwestern, central and southeastern regional Ministry of the Environment Offices

** Shorter slope lengths normally were associated with higher slope gradients longer slope lengths had more gradual slope gradients

Figure 3.3.3: Concentrated Surface Water Flow Causing Gully Formation Along the Steep Side Banks

Figure 3.4.1: Sediment deposition at the base of a Landfill Cap.

4.0 MODELLING THE EROSION PROCESS ON LANDFILL SITES

The site visits emphasized the fact that interrill and rill erosion is not the only form of water erosion, nor is surface water running down a slope the only erosion mechanism to be modelled on landfill sites. For example, some of the gullies oriented up and down the slopes, in some cases, appeared to be the result of erosion down preferential flow paths caused by compaction by the equipment used to place the cover. In other instances, it appeared that once water infiltrated the landfill cap it could not necessarily be eliminated from the possibility of contributing to erosion. This infiltrated water could become subsurface flow as it follows the relatively impermeable cap layer beneath the topsoil reappearing as seepage at locations of thinning of the soil cover where it again can act as surface flow and thus the transport medium for the erosion process.

Another dominant mechanism seemed to be the result of collapse of the fill underlying the cover along with subsequent enlargement of the hole. The upper walls of these holes were severely undercut with what appeared to be subsurface seepage. Some of these holes were completely unconnected to downstream holes. It appeared that downslope flow through the upper layers of the cover might be an important flow mechanism and that disruption of the cover by collapsing underlying fill could contribute to erosion of landfill covers.

With the exception of erosion problems generated by fill material collapsing underneath the structure, similar mechanisms for erosion can be found on agricultural land. The relative magnitude of erosion problems and losses caused by groundwater seepage as opposed to surface water runoff is not as high on agricultural land as would appear to be the case with landfill cover erosion. This would explain the lower emphasis placed on this loss mechanism. Models such as the USLE and even more physically based relationships do exist to model erosion due to overland flow. A review was made of some of these available models, their values and deficiencies, and will be included in the final report for this phase of the study.

Being able to model infiltration on a landfill cover would appear to be a very important component. Unfortunately, no models presently exist which can model such phenomenon as cracking of the cover, downslope seepage through a cover and the effect of frost layers during snowmelt which reduce infiltration.

5.0 PRELIMINARY INVESTIGATION OF INFILTRATION INTO LANDFILL COVERS

5.1 Background

Having the capability to physically quantify that portion of rainfall that infiltrates and percolates through a landfill cover as opposed to becoming overland runoff would be advantageous when attempting to model the erosion process on a landfill site. In 1987, personnel within the Waste Management Branch of the Ontario Ministry of the Environment developed a lysimeter design, six prototypes of which were subsequently installed by the Region of Peel on a decommissioned area of the Brittania Road Sanitary landfill site located in Mississauga. A cross-section of the lysimeters as they were installed at the site is presented in Figure 5.1.1. Following installation, the tasks of monitoring and evaluating the performance and results obtained from the lysimeter was transferred to the study team. It was anticipated that through monitoring the lysimeters, an improved understanding of the infiltration component of the entire erosion process on landfill covers would be possible.

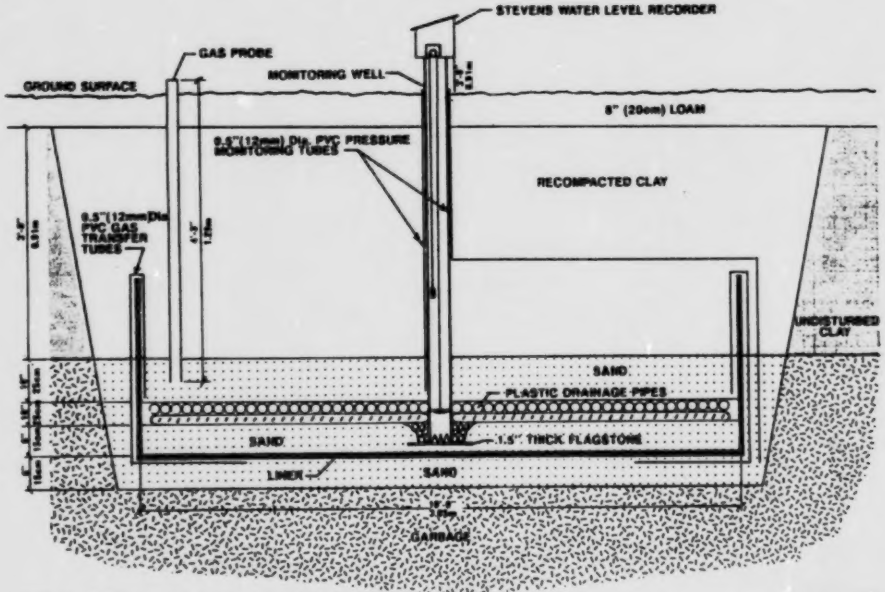
5.2 Experiences with Lysimeters to Date

Leupoid-Stevens stage recorders were installed on each of the six lysimeters in August 1987. In September the calibration procedure was defined and initiated. The objective of the calibration procedure was to measure changes in the depth of water in the lysimeters storage zone caused by a known input volume with a view to generating a percolation volume verses depth curve. If successful, this data would ultimately be employed to determine what fraction of precipitation percolates through the landfill cap. Day one of the calibration procedure progressed much as expected. A datum was defined, inputs were added in increments of 100 litres and static levels were recorded following each addition. When inputs were approximately equal to the capacity of the storage zone a stage recorded was reinstalled to monitor the final steps to equilibration. The following day the level in the first lysimeter which was calibrated was measured and recorded. The entire procedure was repeated and again appeared satisfactory. Upon returning one week later, it was observed that the recorder charts had fluctuated up and down the chart considerably and, at the time, inexplicably given that there could be no losses from the storage zone. For the next few weeks, theories and counter-theories were discussed and dismissed. Eventually it was hypothesized that atmospheric pressure was influencing the recording level in the monitoring well, more specifically, an inverse relationship existed where high barometric pressures resulted in low water levels and conversely where low barometric pressure yielded high water levels. As can be seen in Figure 5.2.1 the inverse correlation between barometric pressure and recorder (water) level were too strong to dismiss. For the above hypothesis to explain the extreme fluctuations in water level readings, the presence of a trapped air layer between the rising water level and the apparently impermeable or, at least, semi-impermeable overlying recompacted clay layer was essential. To confirm or deny the existence of the "bubble zone", holes 6 cm in diameter were drilled from the surface down through the recompacted clay layer to vent the lysimeters. ABS pipes were installed in the vent holes and the lysimeters were again left with stage recorders installed. While not conclusive, the results of the next monitoring period indicated the hypothesis of the trapped bubble to be correct. Vented lysimeters reacted favourably and indicated similar remedial action was warranted for the balance of the lysimeters. Rather than venting from the surface, numerous small holes were drilled into the well casing in the 0.8 metre zone above the well bottom (see Figure 5.1.1). Holes in the well casing also facilitated a rapid exchange of air and water, eliminating unnecessary delays waiting for the lysimeters to equilibriate during calibration.

The success of the aforegoing remedial drilling resulted in six out of six lysimeters functioning according to design, at least as far as the soil physics is concerned. Figure 5.2.2 illustrates a recent period of recording

FIGURE 5.1.1 :

Drain Tile Lysimeter Cross-Section


STEVENS WATER LEVEL RECORDER
GAS PROBE
MONITORING WELL
GROUND SURFACE
8" (20cm) LOAM
0.5"(12mm) Dia. PVC PRESSURE MONITORING TUBES
RECOMPACTED CLAY
0.5"(12mm)Dia PVC GAS TRANSFER TUBES
UNDISTURBED CLAY
SAND
PLASTIC DRAINAGE PIPES
SAND
1.5" THICK FLAGSTONE
LINER
SAND
GARBAGE

NOTE: Gas monitors and equalizers installed in 2 of 6 lysimeters

Not to scale

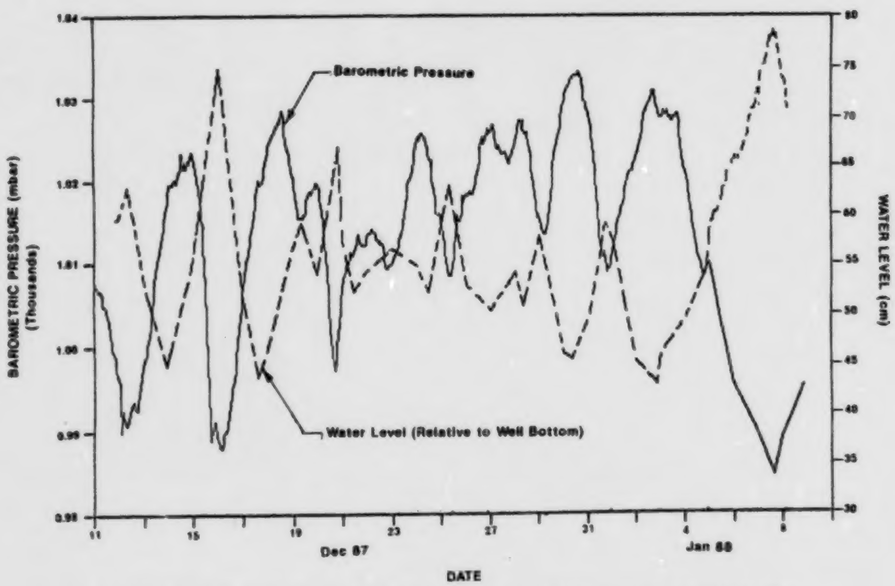
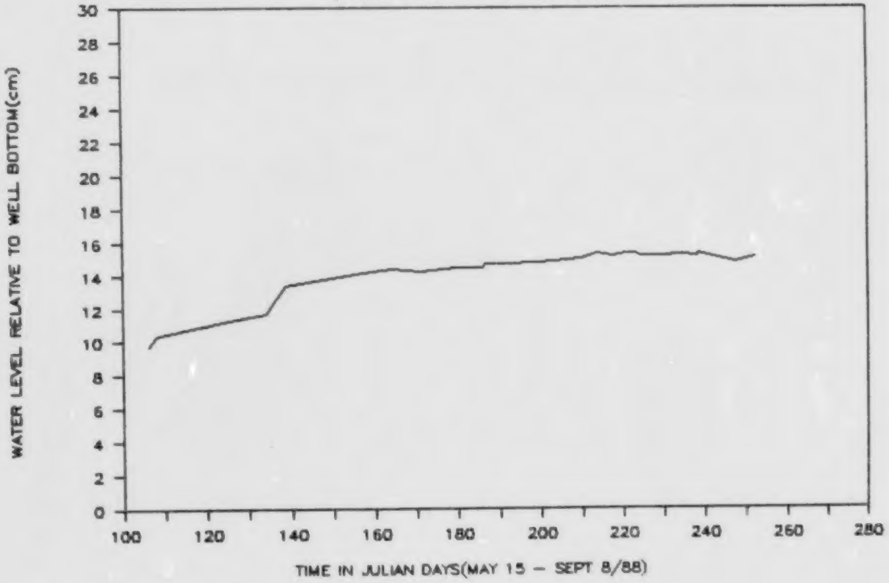


FIGURE 5.2.1: COMPARISON OF BAROMETRIC PRESSURE AND WELL WATER LEVEL

FIGURE 5.2.2: WELL WATER LEVEL

(AFTER VENTING – LYSIMETER #4)



and, as can be seen, the water levels are rising slowly or remain relatively horizontal. With the lysimeters now functioning more as would be expected they were again calibrated in the summer of 1988 to develop depth versus storage volume curves.

Some concern was raised by the designers of the lysimeters as to their possible deterioration. Consequently two (2) lysimeters (one of each storage zone type) were excavated in the summer to determine their condition. Pertinent lysimeter layers were not surveyed in and referenced to a permanent benchmark, making it difficult to conclusively determine if any shifting of the lysimeter had taken place. Nevertheless, based on our interpretations as to how they were installed, it was concluded that little change had occurred in their configuration since their installation.

Minor problems still persist with respect to obtaining continuous reliable datasets from the lysimeters. Recommendations for improvements which are based on experiences to date with the lysimeters as they currently exist have been made. Such changes, if implemented, would alleviate most of these minor problems and thus enhance the lysimeter's functioning.

6.0 CONCLUSIONS

From the site inspections made to landfill sites in southern Ontario, it would appear that soil erosion caused by water is a problem and without attention given to this problem upon closure of the site could affect the long-term stability of the landfill cover. Landfill covers are most susceptible to erosion during the first few years after being decommissioned. Establishing a vegetative cover early and quickly while managing surface water flow off the site would appear to be key factors. On the basis of the observations made at several landfill sites, it appears that erosion is fairly easy to control and contain within reasonable limits. Increased adoption of and slight modifications to erosion control planning techniques and practices currently used on agricultural land and road right-of-ways would, in the majority of cases, produce quite satisfactory results in terms of controlling the landfill cap erosion observed.

Being able to quantify the amount of infiltration would be beneficial not only in terms of more accurately estimating erosion losses from landfill covers but also for estimating what portion of yearly rainfall percolates through the cap generating leachate. The prototype lysimeters which were tested have had numerous problems associated with them, and could yet be improved. Consequently, the data from them at the time of writing is inconclusive. A full year of data will better answer the question as to their ability in estimating landfill cover infiltration.

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C17

DEVELOPMENT OF BACKFILL AND CONSTRUCTION APPLICATION GUIDELINES FOR ONTARIO

by

M. Kelleher and B. Whiffin
CANVIRO Consultants
A Division of CH2M HILL ENGINEERING
Plaza 3, Suite 100, 2000 Argentia Road
Mississauga, Ontario L5N 1V9

Tentative guidelines were developed for the classification of industrial waste and by-product materials for backfill and construction applications. These tentative guidelines were based on results of bulk characterization of the material in question, and also on leachate extraction procedure results. A tentative classification system was developed, based on the above two procedures. The effectiveness and reliability of these tentative guidelines are currently being tested through a field program which examines the impact of industrial materials used in backfill and construction applications. Three materials are being investigated during this phase of the project, namely; blast furnace slag, fly ash and foundry sands. Sites which contain relatively large volumes of each of these materials were selected for a field study program. The program involves a hydrogeological investigation of each site, bulk chemical characterization of the material placed at the site, and a leachate extraction procedure carried out on the material placed at the site. Groundwater both upstream and downstream of the site is analyzed. The purpose of the field study is to assess the extent to which results of the bulk chemical characterization and leachate tests are an indication of the impact of material placement on downstream groundwater quality. The results of the field program will determine the effectiveness of the tentative guidelines, which will then be modified, as appropriate, based on the field program results.

DEVELOPMENT OF BACKFILL AND CONSTRUCTION APPLICATION GUIDELINES FOR ONTARIO

INTRODUCTION

Historically, selected industrial waste and by-product materials such as slags, fly ash and foundry sands have been employed for backfill and in a variety of construction uses. Decisions regarding specific applications have been made on an ad hoc basis with varying amounts of supporting data. The lack of standard procedures for assessing and classifying these wastes prompted the Ontario Ministry of the Environment through its Waste Management Branch to undertake preparation of Guidelines for the Utilization of Industrial Wastes in Backfill and Construction Applications.

A tentative waste classification process was developed during Phase I of this project. A second phase program was developed to establish the effectiveness and reliability of the proposed guidelines developed in Phase I, through field studies at selected sites.

The site selection process was based on evaluation of known sites which were ranked on a number of criteria with high, medium and low ranking scores. Field testing involved bulk quality characterization and leachate testing of backfill samples from each of the selected sites. Hydrogeologic investigations were also conducted at the selected sites and included groundwater sampling for a number of parameters.

The proposed guidelines will be modified as required, based on the results of the Phase II field investigations.

PROPOSED CLASSIFICATION PROCESS

The proposed classification process was derived from a number of Ontario Regulations in existence at the time of classification process development. Three disposal categories were recommended, namely:

- Lakeshore/Shoreline Disposal
- Restricted Land Use
- Construction Use

The classification of a waste material into one of the above categories would be based on results of bulk quality and leachate characterization tests. A fourth category, immobilization, referred to the further processing of waste material to produce a new material requiring re-classification.

A "Schedule of Acceptable Wastes and Uses" was also recommended in which industrial materials would be included by common name and description, along with the use category for which the waste is considered acceptable. Wastes listed in the Schedule would not normally require bulk chemical characterization or leachate quality testing, although the MOE at its discretion may wish to review the material use in a particular situation, and request additional testing.

FIELD PROGRAM SITE SELECTION

The initial field studies were limited to the following materials:

- blast furnace slag
- fly ash
- foundry sands

An inventory of sites in Ontario containing these materials was developed, and each site evaluated using a number of project specific criteria. A short list of desirable sites was developed, and each site assessed in some detail to determine its suitability for the proposed study. Desirable criteria included:

- Site contained only one material
- Geological and hydrogeological setting were known
- Site was still operational/relatively new
- Site boundaries and operational history were documented
- Site was typical of other sites containing same material

The final site selection process was more complex than originally envisioned for a number of reasons. A number of sites containing blast furnace slag were identified, however, most of these were a number of years old. The impacts of slag placement are reportedly more significant soon after placement, hence a younger slag site was preferable. However, because of the demand for slag in recent years in the cement and concrete industry very few recent slag sites were identified.

A number of sites were potentially affected by surrounding land use (e.g. slag in sewer backfill, or beneath roads, foundry sand adjacent to sewage sludge, etc.). Little or no hydrogeologic or geologic information was usually available for the sites identified. In some cases (e.g. foundries) waste properties varied within the same industry. Foundry sand sites were frequently found to contain a heterogeneous mix of waste materials from foundry operations. It became difficult to identify a site with one type of material only.

Other problems encountered included the difficulty of identifying an active site, and also obtaining property owners permission to carry out field work. Many site operators gave verbal approval to site work during preliminary discussions, but decided against co-operation when written approval was requested. Because of the above difficulties, site selection took longer than originally anticipated. Field work was finally carried out during spring, summer and fall, 1988 at three sites described in the following sections.

FOUNDRY SAND SITE

The foundry sand site is located outside Hamilton, Ontario, and disposal is on-going in a marshy area, which is being reclaimed. The site covers several acres and has been operational since 1979, and has a Certificate of Approval. The depth of sand is 1.3-2 m. Shell core and green sands are used at this grey iron foundry. A total of 4 piezometer nests (2 piezometers at each) were located at the site, at depths of up to 7 m. One recent and one older foundry sand sample were taken for leachate testing and bulk chemical characterization.

FLY ASH SITE

The fly ash site is located in parkland in Mississauga, and has been closed since 1978. Extensive monitoring was carried out at the site over a number of years by others. Existing wells were re-conditioned for the present study. One sample of recently produced ash was taken for bulk and leachate testing from the generating station which supplied the ash for the site originally. A second sample of weathered ash was taken from the site itself for similar analyses. The results of these analysis will determine if the ash characteristics change with time by comparing recent and weathered ash results. A total of 8 piezometers at the site were sampled for the present project. Two of these were located in the ash itself. The remaining piezometers were located in native soils upgradient, beneath and downgradient of the site.

BLAST FURNACE SLAG SITE

The blast furnace slag site is a highway ramp located in Mississauga, where slag was used as a foundation for a bridge abutment constructed approximately two years ago. The slag is up to 5 m deep at some parts of the ramp embankment. A total of 10 piezometers are located at the site, to a maximum depth of 10 m. Weathered slag samples for bulk chemical and leachate testing were taken from the ramp, and a fresh slag sample was taken from a slag company in Hamilton. Groundwater samples were collected from 8 of the 10 piezometers.

DESCRIPTION OF SITE INVESTIGATIONS

Site investigations consisted of:

i) Hydrogeologic investigations
ii) Groundwater sampling and analysis
iii) Backfill material sampling and analysis

One or two background wells were installed upgradient of each site. Up to seven additional wells were sampled, some within the wastes, some below the wastes, some downgradient of the wastes. Parameters analyzed in groundwater taken from these wells generally included trace metals, major ions (including alkalinity), phenols, electrical conductivity temperature and pH. Hydraulic conductivity, was evaluated using in-situ hydraulic testing. Groundwater flow direction and velocity will be determined as part of the study.

The groundwater sampling effort was directed at obtaining representative samples. Extensive well development and testing was conducted prior to each sampling. Dedicated samplers were used for the project. Samples were filtered and prepared in the field where necessary. A minimum of three well volumes were extracted prior to each sampling round.

QA/QC (Quality Assurance/Quality Control) measures in the field consisted of a trip blank and a duplicate for each site during each of three sampling rounds.

Backfill material sampling and analysis consists of taking both old and recent ("fresh") samples of material for leachate (Regulation 309 Procedure) and bulk property testing.

INTERPRETATION

Classification of samples will be carried out in accordance with the draft guidelines. The impact on groundwater quality will be determined by comparing upgradient and downgradient results. The observed impact on groundwater will be compared to drinking and surface water guidelines.

The results of the field program will be used to judge the effectiveness of the tentative guidelines, which will then be modified, as appropriate, based on the field program results.

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C18

STEMMING THE RISING TIDE OF WASTE

Moderator:	Don Mackay University of Toronto
Members:	Colin Isaacs Pollution Probe Inc.
	Romeo Palombella Government Refuse Collection and Disposal Association
	Hardy Wong Environment Ontario

The panel discussion will be recorded and transcribed. A printed copy can be obtained upon request from:

Ministry of the Environment
Research and Technology Branch
135 St. Clair Avenue West,
12th Floor
Toronto, Ontario
M4V 1P5
(416) 323-4574

SESSION C

LIQUID AND SOLID WASTE RESEARCH

Poster Presentations

CP1

RETRACTABLE COMPOSITE ADSORBENTS FOR ENVIRONMENT CLEAN-UP.

B.Gillies*, E.Stubley, I.Treurnicht and L.Read, EcoPlastics Ltd.,Willowdale, Ontario M2H 3B4
O. Meresz, Ministry of the Environment, Rexdale, Ontario M9W 5L1

EXTENDED ABSTRACT NOT AVAILABLE

CP2

ABSTRACT

TREATMENT AND DISPOSAL OF HAULED SEWAGE UNDER PART VIII, ENVIRONMENTAL PROTECTION ACT.

J.L. Smith, M.Sc., of Oliver, Mangione, McCalla & Associates Limited
154 Colonnade Road South
Nepean, Ontario
K2E 7J5
(613) 225-9940

Introduction and Objectives

The firm of Oliver, Mangione, McCalla & Associates was commissioned by the Ministry of the Environment to study the treatment and disposal of hauled sewage across the province of Ontario.

The first objective in this study was to establish the current practices of hauled sewage treatment and disposal. To collect this data, a questionnaire was devised and submitted to each of the Health Units and Ministry of the Environment Regional and District offices. The questionnaire collected data on: (i) hauled sewage collection including haulers, vehicles and annual volumes; (ii) hauled sewage composition; (iii) disposal and treatment practices and; (iv) complaints and problems. As part of this objective to establish current practices, site visits and interviews were organized with some of the Health Units and Ministry of the Environment offices. These visits included on-site assessment of current disposal systems and allowed for the collection of septage and soil samples. The samples were subsequently analysed for both quantitative and qualitative characteristics to determine the nature of the materials.

The second task in this study was to perform a literature review. This included a review of the Ontario regulations and practices as well as those of adjacent provinces and states. Several databases at the National Research Council of Canada were accessed for references.

The final objective of the study was the assimilation of data and draft reporting of current Ontario practices. The reporting led to recommendations for alternative schemes for the treatment and disposal of hauled sewage.

Current Practices

The study results indicated that approximately 450 haulers are operating some 560 vehicles across the province, and collected an estimated 900 million litres of hauled sewage last year. The average haul distance to the disposal site is 27 kilometer and the average haul fee is $68.00.

This septage is being disposed in a reported 628 sites across the province, two-thirds of which are agricultural disposal sites (423 sites). The majority of the agricultural sites were reported to be using a moving truck to spread hauled sewage (362 sites). The remaining disposal sites are primarily municipal wastewater treatment plants (81 sites) and lagoon systems (64 sites). All of these disposal methods were reported to be used during the winter months, as 255 sites were reported operational.

The majority of complaints received by the Health Units and the Ministry of the Environment offices concerned disposal sites, approximately 300 over the past year. These complaints were primarily about site pollution including surface and groundwater pollution as well as aesthetic concerns including site odours and health risks. A reported 100 complaints were received about the sewage haulers, the majority of which were concerned about unauthorized dumping, and the balance of which were primarily about traffic concerns.

Treatment and Disposal Options

A literature review was conducted to assess the current treatment and disposal options in North America. The following treatment alternatives are available:

1) Co-treatment of septage and sewage
   Wastewater Treatment Plants
2) Land Application - land spreading and soil injection

3) Lagoons and Stabilization Ponds
4) Chemical Treatment
5) Rotating Biological Contactors
6) Composting
7) Conditioning
8) Dewatering
9) Disinfection

There are several disposal alternatives available for hauled sewage, these include the following:

1) Surface Application
    a) land spreading
    b) ridge - furrow
    c) spray irrigation

2) Subsurface Application
    a) plow - furrow
    b) sub-sod injection
    c) terreator injector

3) Burial Methods
    a) trenches
    b) sanitary landfills
    c) leaching lagoons
    d) disposal lagoons

Conclusions and Recommendations

At the time of publication the conclusions and recommendations have not been completed for this study.

CP3

FACTORS AFFECTING THE CONCENTRATION OF METAL IONS IN MUNICIPAL REFUSE LEACHATE.

G.Kosta, S.Pirani and D.W.Kirk Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario M5S 1A4.

The use of landfill has been the traditional means of disposing of municipal refuse and remains the most economical and attractive disposal option. Despite the long history of this form of disposal, much remains unknown of the processes that occur in the refuse site. The effects of toxic contaminants in municipal refuse is of particular concern since migration of these species to the environment might occur. Factors which affect the migration of contaminants are complex and include: the variable nature of refuse, the infiltration of moisture from precipitation, the microbial breakdown of organic matter, the generation of an anaerobic environment and the temperature fluctuations. One of the major difficulties in assessing the impact of a municipal refuse site on the environment is in predicting the quantity and contaminant levels of the leachate produced.

The leachate generated from a municipal refuse landfill begins as precipitation and undergoes a number of changes as it percolates through the landfill environment. The initial air saturated water becomes increasingly anaerobic and becomes loaded with both inorganic and organic species before seeping into the water table. The impact of this liquid on the environment is determined by the volume discharged and the concentration of species in the liquid. Predicting the concentrations of metal ions in the leachate is very difficult due to the nature of the refuse and the reactions taking place in the landfill.

One approach in determining the composition of the leachate is to identify the relative importance of the various factors in controlling the amounts of the contaminants. In this work, we studied the concentration constraints that might occur because of the presence of carbonate and hydroxide species. Many metals have sparingly soluble salts of carbonates or hydroxides, so that there might be a natural limit to the concentrations of these species found in municipal refuse leachate.

The assumptions that were used in testing this hypothesis are that the biological breakdown of organic matter to CO_2 cannot produce a pressure of more than one atmosphere (101 kPa). This gas pressure would set the maximum dissolved CO_2 concentration and can be calculated from gas law solubilities. This dissolved CO_2 would equilibrate to form the carbonate and bicarbonate ions (dependent on the pH of the leachate) and in turn limit the concentrations of some of the dissolved metal ion species. This approach assumes that the liquid and solids are in contact sufficiently long to establish a pseudo-equilibrium state. While maximum concentrations of metal ions can be calculated, many additional factors could prevent concentrations from reaching these values. However, concentration values cannot exceed the solubility limits unless the metal ion is in a complex, more stable than the carbonate/bicarbonate/hydroxide salts. Identification of these very stable metal complexes is particularly important because the complexes are likely to be organic in nature and hence able to be assimilated in the food chain. Thus maximum metal ion concentrations that can be predicted through solubility laws, can be modelled for worst case scenarios, while metal ion concentrations that exceed solubility predictions should be targeted for their impact on the biosphere because of their potential for bioaccumulation.

The metals that have been investigated include: calcium, lead, zinc, iron and cadmium. The data from column studies on the effect of codisposal of industrial wastes with municipal refuse was used as the source of metal ion concentrations as a function of pH. These studies have been reported elsewhere[1]. All the metals studied showed concentrations less than that predicted by solubility modelling except iron. In general, a good correlation with solubilities based on carbonate for pH ranges 5 to 8 was observed, while hydroxide solubilities yielded less accurate predictions. Conversely, for a pH ranging from 9 to 12.5, predicted concentrations based on hydroxide solubilities were closer than those predicted by carbonate solubilities. The formation of stable organic zinc complexes reported by Pohland and Gould[2] were not observed in this work, despite the significant zinc concentrations of industrial waste used in some of the tests.

The iron concentrations observed were interesting because they exceeded the solubility limits expected for the given pH and carbonate levels. Since all of the samples were from filtered leachate (<0.45um) the possibility of microbial or suspension interference is low. The solubilized iron was sensitive to oxygen which caused precipitation in leachate samples exposed to air. The evidence points to the presence of an organic complex of iron. Since the complex is unstable in the presence of air, the mobility of the species is likely to be limited.

The significance of the research is that a variety of metal ions which are found in municipal refuse leachate appear to be adequately modelled through solubility limitations imposed by carbonate and pH conditions. The presence of an organic iron complex in municipal refuse leachate is an important finding since the concentration limits imposed by carbonate and hydroxide conditions do not apply. This species may have implications for bioaccumulation.

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CP4

SLOW RATE INFILTRATION LAND TREATMENT AND RECIRCULATION OF LANDFILL LEACHATE IN ONTARIO

R.A. McBride, A.M. Gordon, P.H. Groenevelt, T.J. Gillespie, and L.J. Evans
University of Guelph, Guelph, Ontario

1.0 Introduction

This extended abstract reports on progress made up to the approximate mid-way point of this three-year research study (M.O.E. project no. RAC-333). Emphasis will be placed on two specific studies being undertaken in this multi-faceted, interdisciplinary project; that is vegetative and soil microbial response to MSW leachate exposure. The vegetative response data presented here originate from the Muskoka Lakes landfill near Port Carling, Ontario (McBride *et al*., 1988), whereas the soil microbial response data were collected at the Hamilton-Wentworth regional landfill in Glanbrook Township. In all, four leachate sources are being used for various experiments in this study, and Table 1 provides information on certain chemical constituents of each. A full screening of organic contaminants is also being carried out in collaboration with the Canada Centre for Inland Waters in Burlington, Ontario.

Table 1. Chemical composition of four landfill leachates under investigation.

Chemical Constituents*	Landfill Site			
	Muskoka	Glanbrook	Leamington	Guelph
NO_3	0	0	0.34	0
NH_4	103	12.5	360	865
PO_4	0	0	0	1.38
SO_4	0	258	10.0	49.4
Cl	98	1039	900	2464
Mg	32	594	90	580
K	114	406	483	1301
Na	41	580	373	1109
Fe	37.5	0.22	0.42	1.11
Mn	6.77	0	0.01	5.07
Ni	1.46	0	0	0.52
Cd	0.12	0.03	0.06	0.05
Cu	0	0	0	0
Pb	0	0	0	0
Zn	2.67	0.04	0.05	0.03
TOC	2446	447	216	3774
pH	5.44	7.45	7.65	7.01

* all chemical constituents are in units of $\mu g \bullet ml^{-1}$ with the exception of pH

2.0 Vegetative Responses

2.1 Preface

Research on vegetation at the Muskoka Lakes landfill site has been directed at aspects of forest decline and the stress ecophysiology of sugar maple (*Acer saccharum* Marsh) attributable to the leachate spray irrigation system operated by the municipality. Studies on the carbon dioxide and water vapour exchange rates of understory saplings and the spectral properties of their leaves have been undertaken in irrigated and unirrigated areas. The spectral properties of overstory leaves of mature trees pruned above the range of direct foliar contact have also been investigated in collaboration with researchers from the Ontario Centre for Remote Sensing (OMNR). Data from the 1987 and 1988 seasons are being analysed and some preliminary results are presented and discussed here.

2.2 Understory Photosynthesis and Transpiration

Daily spray application of leachate on the forest understory during the growing season deposits a residue on plant leaves to the point where the entire adaxial (upper) surface is irreversibly stained through to leaf senescence in the autumn. This precipitate has properties that may instigate changes in leaf energy budgets by altering the amount and characteristics of incident radiation in addition to possible direct phytotoxic effects or changes in leaf cell structure. The abaxial (lower) surfaces of the leaves, however, remain largely unstained, the leaves remain turgid and otherwise retain the outward integrity of unsprayed leaves throughout the growing season.

A LI-COR model LI-6000 portable photosynthesis system was employed to determine carbon dioxide and water vapour exchange rates and stomatal conductance. Measurable decreases in the stomatal conductance and photosynthetic rates of spray irrigated saplings were observed (Figure 1). Photosynthetic rates of spray irrigated saplings also decreased with increasing PAR irradiance (Figure 2) in contrast to the normal rise with irradiance demonstrated by the control saplings. The rate at which photosynthesis increased in response to higher stomatal conductance levels is also lower in irrigated saplings (Table 2) but appears to have improved over the two month sampling period in 1988. In contrast to these findings, transpiration rates of spray irrigated saplings did not deviate substantially and, in some cases, actually exceeded those measured in control saplings.

Many environmental parameters have an effect on stomatal conductance (e.g. relative humidity, irradiance, leaf and ambient air temperatures) and some of these factors have a direct effect on the photosynthetic process itself quite apart from the influence on CO_2 fixation through stomatal aperture response. The relative importance of any one parameter in controlling photosynthetic rates may be more easily discerned if viewed in terms of its inhibitory effect (i.e. photosynthetic limitation). This enables the partitioning of stomatal and non-stomatal limitations to photosynthesis (Jones, 1985). This approach has been applied to distinguish parameter limitations to photosynthesis in trees under differing environmental conditions (Teskey *et al*., 1986) and during rapid water stress

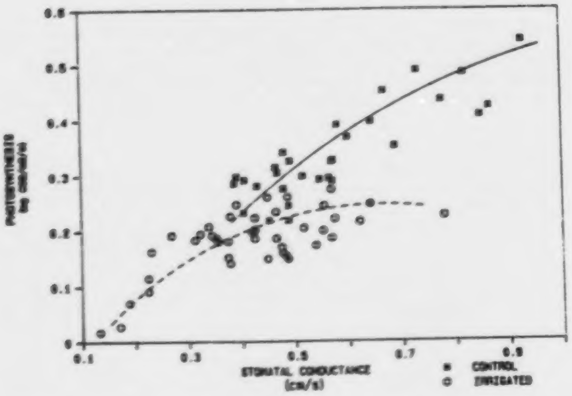

Figure 1. Rate of photosynthesis vs. stomatal conductance for leachate irrigated and unirrigated understory leaves of sugar maple at Muskoka Lakes (Aug. 31, 1988).

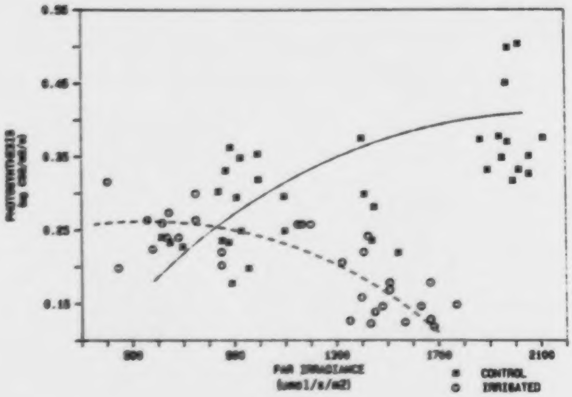

Figure 2. Rate of photosynthesis vs. incident photosynthetically-active radiation for leachate irrigated and unirrigated understory leaves of sugar maple at Muskoka Lakes (Aug. 16, 1988).

(Cornic *et al.*, 1983). The lower rates of photosynthesis in spray irrigated saplings compared to those of control saplings at similar stomatal conductances (Figure 1) and the generally lower rates at which photosynthesis increases with larger stomatal apertures (Table 2) infer that the dominant photosynthetic limitations in operation may be non-stomatal in nature.

Table 2. Results from simple regression of photosynthetic rate ($mg\ CO_2 \bullet m^{-2} \bullet s^{-1}$) of sugar maple against the logarithm of stomatal conductance ($cm \bullet s^{-1}$) for three dates.

		Least Squares Parameter Coefficients*	
Date	Treatment	b_0 (intercept)	b_1 (slope)
July 6, 1988	Control	0.429	0.154
	Irrigated	0.254	0.081
August 16, 1988	Control	0.432	0.153
	Irrigated	0.303	0.112
August 30, 1988	Control	0.451	0.205
	Irrigated	0.316	0.144

* all regressions were significant at $P < 0.001$

Water use efficiency (WUE), the ratio of carbon dioxide assimilated to water lost, was lower in irrigated saplings over the sampling period (Table 3). However, the later measure of irrigated WUE exceeds that of the earlier season control measure made under abnormally severe water stress conditions.

Table 3. Water use efficiency of irrigated and unirrigated sugar maple for three dates.

Date	Treatment	Water Use Efficiency
		$mg\ CO_2 \bullet g^{-1} H_2O$
July 6, 1988	Control	3.21 ± 0.05
	Irrigated	0.94 ± 0.37
August 16, 1988	Control	6.64 ± 1.32
	Irrigated	0.87 ± 0.42
August 30, 1988	Control	13.14 ± 1.50
	Irrigated	4.87 ± 0.68

2.3 Understory and Overstory Leaf Spectral Properties

The quality and quantity of spectral reflectance, transmittance and absorbance of light by leaves in the visible and near-infrared (400-1100 nm) wavelengths provide a basis for characterizing foliar structure and symptomatic interpretation of plant health (Gates et al., 1965; Horler et al., 1983). Spectral measurements on understory and overstory leaves were made with a LI-COR 1800 portable spectroradiometer fitted with an integrating sphere. Measurements of overstory leaves were also performed by O.C.R.S. personnel using a Spectron 590 spectroradiometer.

The control data for adaxial spectral reflectance of understory sugar maple (Figure 3) provide a typical pattern, with the characteristic green "thumbprint" at 540 nm (i.e. chlorophyll, nitrogen content), the "chlorophyll well" at 680 nm, and the "red edge and shoulder" at 700-1100 nm (i.e. indicator of stress, cell structure integrity, water content). At positions closer to the spray nozzles, the amount of leachate intercepted and the density of residue precipitated on the leaf surfaces increases, progressively altering the spectral reflectance. The reduced reflectance of the sprayed leaves in the red (700-1100 nm) waveband suggests a higher absorbance, possibly upsetting the normal leaf energy balance and leading to higher leaf temperatures. Spectral reflectance curves for understory abaxial leaf surfaces (Figure 4) are not as drastically altered and the decreased green reflectance (540 nm) is indicative of increased nitrogen and/or chlorophyll content (Hinzman et al., 1986; Shibayama and Akiyama, 1986).

The two instruments used in the spectral study of overstory leaves concurred well in general reflectance measurement. Reflectance patterns generated by the LI-COR 1800 for leaves of control and irrigated trees in July and August are presented in Figure 5. In July, virtually no differences in reflectance could be discerned, but similar spectra from August for irrigated trees demonstrate a decreased reflectance in the 540 nm range and increased reflectance in the red range. The "blue shift" of the red edge of reflectance that has been reported elsewhere (Horler et al., 1983; Rock et al., 1988) as being indicative of forest decline was not evident from overstory spectral measurements during the 1988 field season at Muskoka Lakes. This lends further support to the assertion that over-irrigation of leachates during abnormally wet seasons (e.g. 1986) is likely to be the most important factor contributing to the forest die-back observed at this landfill site (McBride et al., 1988).

3.0 Soil Microbial Responses

Two plot-scale installations (factorial, RCB experimental design) involving three irrigation methods (spray, trickle, subsurface for leachate, spray only for water) and three application rates (3.5, 7.0 and 14.0 $mm \cdot d^{-1}$) are operational at the Glanbrook landfill. A third is situated at the Essex County landfill #2 near Leamington.

Figure 6 shows a respresentative set of soil respiration data collected from the plots of the forested site at the Glanbrook landfill in 1988. The Glanbrook soils belong to the Smithville catena and are comprised of about 55% clay (dominantly clay mica/vermiculite, unbuffered C.E.C. 52 $cmol \cdot kg^{-1}$, specific surface 250 $m^2 \cdot g^{-1}$). The application of raw leachate to the forested plots significantly increased the measured soil respiration when compared to both the water irrigated plots and the environmental (rain-fed)

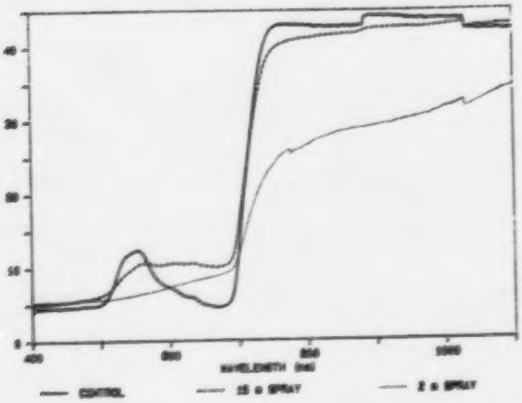

Figure 3. Spectral reflectance patterns for adaxial surfaces of leachate irrigated (variable intensity) and unirrigated understory leaves of sugar maple at Muskoka Lakes (Aug. 31, 1988).

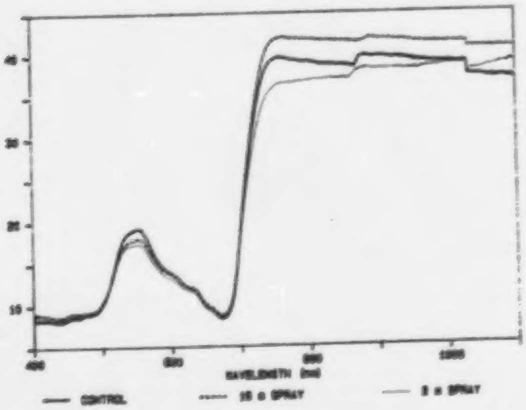

Figure 4. Spectral reflectance patterns for abaxial surfaces of leachate irrigated (variable intensity) and unirrigated understory leaves of sugar maple at Muskoka Lakes (Aug. 31, 1988).

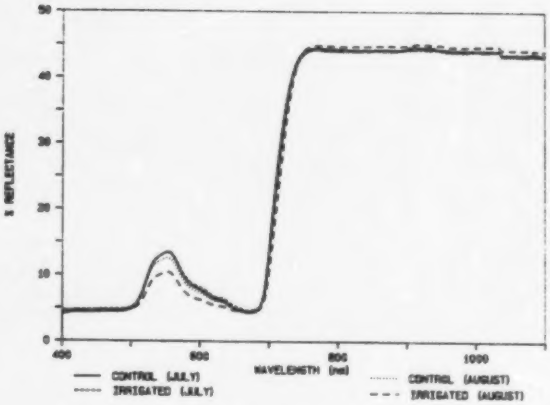

Figure 5. Spectral reflectance patterns for adaxial surfaces of overstory leaves of sugar maple trees situated within and outside of leachate irrigation areas at Muskoka Lakes (July 6 and Aug. 16, 1988).

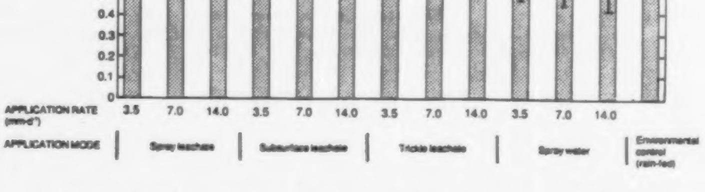

Figure 6. Rates of soil respiration on all treatment plots at the forested irrigation installation at the Glanbrook landfill (Aug. 31, 1988).

control ($P < 0.0001$). This analysis of variance takes both the rate and mode of irrigation into account. Soil respiration on plots receiving leachate by the spray method was significantly lower when compared to the trickle and subsurface leachate irrigation plots ($P < 0.0001$). For the trickle and spray leachate treatments, soil respiration tended to increase with the quantity of leachate applied while the opposing trend was observed in the subsurface irrigated plots. The application of water to the plots by spray irrigation significantly decreased soil respiration when compared to the environmental control ($P < 0.0001$).

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CP5

ESTABLISHING VEGETATION ON EROSION-PRONE LANDFILL SLOPES IN ONTARIO

Tom W. Hilditch*, Christopher P. Hughes

INTRODUCTION

Landfills are used in Ontario for the disposal of waste materials. Sites can accept wastes from municipal, commercial and industrial sources, depending upon their licence restrictions. Owned by either public or private operators, landfills vary in size from less than a hectare to over 50 ha. The larger sites tend to be those that are closer to major urban areas.

Landfills take one of three general forms in Ontario: a hill or mound, a filled valley, or an excavated trench, backfilled with waste. The mound may have originated in depressions or excavations such as abandoned pits or quarries. Both the mound and valley filling operations can result in steep slopes. The backfilled trench generally results in a flat, final grade.

Intermediate soil cover is required on all waste throughout the operation. The soil cover, upon site closure, is increased with a cap material; generally between 0.5 m and 2 m of clay. A cover of topsoil, where available, is overlain to enhance final landscaping conditions.

The landfill cap is critical to the maintenance of an environmentally safe site. The soil placed on the landfill and, particularly, on the side slopes, both while the site is still operating and after closure, is prone to weathering forces which result in erosion.

Erosion not only results in a loss of soil but also in potential damage to the surface cap covering the refuse. That damage can lead to several problems:

- increased infiltration of rain water will accelerate the production of leachate,
- avenues for the movement of landfill gases and leachate will emerge,

- garbage will be exposed, resulting in an attraction for nuisance animals such as gulls,
- aesthetics will be reduced, and
- there will be additional costs for the repair of the damaged cap.

BACKGROUND

The Ontario Ministry of the Environment (MOE) is concerned with the problem of erosion on landfill sites but to-date the extent to which the problem occurs in Ontario has not been documented.

In 1987, the MOE commissioned a 3-year research study, the goal of which is to develop a practical approach to remediate erosion on landfill sites via proper vegetation management. A discussion of the study's main objectives and findings to-date is provided here.

The 3 components of the study are:

- an overview of erosion of landfill sites in Ontario,
- identification of the best revegetation techniques,
- establishment of demonstration plots throughout Ontario.

The work undertaken in each of the study's components is briefly summarized below, up to and including the second-year study progress.

APPROACH

Overview of Erosion on Landfill Sites in Ontario

A questionnaire was distributed to the Abatement Officers at 22 District offices of the MOE. As their responsibility lies with the enforcement of proper landfill management, they were contacted to provide a current objective view on landfill erosion throughout Ontario.

Each participant in the survey was asked to provide:

- a description of their landfill-related responsibilities,
- their views on landfill erosion in their specific district, and
- examples of typical landfills which had the potential to host revegetation demonstration plots.

Responses to the questionnaire provided 52 example landfills. The study team screened this number, down to 24 (4 in each of the 6 MOE Regions) for field investigations.

Field data documenting physical and biological characteristics were collected during September, 1987 for each of the 24 landfill sites. The physical characterization included: collection of soil samples, and observations regarding soil type, depth, grain size, moisture, temperature and compaction. The samples were analyzed for macro nutrients, pH and organic matter. The biological characterization included an assessment of the vegetative condition of each site. Percent vegetation cover, species composition and vegetation health were evaluated. The presence of site disturbances including erosion were rated using a relative scale developed during the testing of field techniques.

Identification of the Best Revegetation Techniques

The questionnaire results provided information about site history and the revegetation approach undertaken. That, in conjunction with field work, provided some indication of what techniques were or were not effective.

Literature from throughout North America was reviewed. Successes and failures were evaluated. The most appropriate techniques for site preparation, planting and maintenance were investigated.

Based on the physical and biological data collected during field investigation of the 24 landfill site, 8 sites were chosen for demonstration plots because of their suitability for the preferred vegetation management techniques identified earlier.

Seven plots were planted in May and June, 1988, the eighth being planted in September 1988. The characteristics of each plot varied with respect to the following parameters:

- site preparation (e.g., tillage, fertilization),
- seeding techniques (e.g., hydroseeding, seed drilling),
- mulching techniques, and
- seed mixes.

There were four plots established in each of the 8 sites, generally covering an area of between 0.5 and 1 ha. The number and location of plots were dictated by the configuration of slopes available for testing.

FINDINGS

Overview of Erosion of Landfill Sites in Ontario

The following summarizes key findings from the questionnaire sent to all MOE District offices.

- there was an 86% response rate,
- all those returned provided specific examples of landfills, on which erosion was a problem and/or there were areas suitable for test plots,
- 73% of the respondents completed the general assessment portion of the questionnaire,
- of those, 56% reported landfill erosion to be a moderate concern and 44% reported it to be a minor concern.

A variety of problems associated with landfill erosion were reported. The exposure of buried refuse and increased remediation costs were cited most frequently. A few districts reported decreased aesthetics, nuisance wildlife problems, siltation of nearby streams and an increase in complaints from the public.

The questionnaire also revealed that the physical character of landfills vary throughout the province. For example:

- landfills are generally covered with either clay or sand, but some districts suggested that the cap was/is composed of whatever material is available (eg. inert industrial waste),
- Southern Ontario landfills (south of Pre-Cambrian Shield) commonly use clay as the cap material,
- North of the Pre-Cambrian Shield, clay is much less available and cap materials are usually sand,
- 63% of the respondents reported that revegetation was either sometimes or never completed after landfill closure
- 37% reported that revegetation was attempted frequently or always. The majority of the revegetation efforts included only grading and seeding. Less than 20% of the districts reported any tillage or fertilization prior to planting. Thirteen percent reported tree planting was also practiced on closed landfill sites.

A summary of some field data collected is provided on Table 1. The 24 sites are separated by MOE region and district. The degree of erosion and vegetative cover entries are based on a relative scale.

Key findings are presented in a series of results-statements.

- 88% of the landfill sites inspected revealed the presence of erosion. The sites that did not, had been closed for several years, and/or did not have side slopes.
- 50% of the landfill sites inspected were open and 50% of the landfill sites inspected were closed.
- 100% of the active landfill sites displayed erosion and 83% of the closed sites displayed erosion.
- The nature of the problem of erosion differed when open and closed sites were compared. The greatest erosion occurred on active sites which were commonly characterized by steep, bare slopes, with scattered growth of volunteer or invading grasses and herbaceous plants. Plants typically occurring included Ragweed (*Ambrosia artemiisifolia*), Chickory (*Cichorym intybus*), Wild Carrot (*Daucus carota*) and Spotted Knapweed (*Centaurea maculosa*).

Erosion on closed slopes appeared to be prompted in some cases by: landfill gas production and resultant vegetation mortality, poor or no vegetation establishment after closure, and leachate seepage.

Identification of the Best Revegetation Techniques

Field results suggest that grading and seeding alone are not adequate to ensure the complete revegetation of landfill slopes.

A review of existing information suggests the best techniques can be grouped under three main headings:

- site preparation,
- planting, and
- maintenance.

Site Preparation

One of the main limiting factors in revegetation success is soil compaction. Surface compaction prevents emerging seedlings from penetrating and establishing. This condition is particularly severe on sites capped with silt or clay but without a topsoil cover. Shallow tillage breaks up that surface layer allowing seedling establishment. Equipment such as the rotary tiller or spike-tooth cultivator are well suited to this work. To limit damage to the integrity of the cap, tillage should be restricted to the upper 15 cm of soil.

Topsoil or other materials high in organic matter (eg. sewage sludge, wood waste, paper sludge), can provide a much improved growing medium. Fertilizer and lime may be required on a site-specific basis depending upon soil conditions.

Planting

Techniques for planting turf include hydroseeding, broadcasting and seed drilling. The effectiveness of each varies by site condition. Hydroseeding for example is particularly suited to very steep slopes where access by tractor is limited.

The material selected for planting is important. This study focused on the establishment of a dense, shallowly-rooted turf which would limit infiltration, thereby reducing the potential for damage to the landfill cap. Species selected for planting included: Smooth Bromegrass (*Bromus inermis*), Redtop (*Agrostis gigantea*), White Clover (*Trifolium repens*) and Timothy (*Phleum pratense*).

Maintenance

The vegetation systems identified in this program were aimed at providing a low maintenance landscape. Mowing in highly visible areas and periodic fertilizing were the two main needs identified.

SUMMARY

Erosion is a problem on both open and closed landfills in Ontario. Along with conditions of compaction and low fertility, surfaces of landfills often have special problems; the production of gases and leachate. Adequate revegetation is part of the answer to reducing the erosion problem. The technology exists to improve on revegetation success in the province. The communication and implementation of that technology is important. Current guidelines do not provide specific advice for final landscaping. Follow-up inspections by the OMOE should be continued beyond a 2 - 5 year horizon. A long term program should be instituted to ensure landfill cap integrity.

The end product of this 3 year investigation, a landfill revegetation manual, will be of assistance in communicating that technology.

ACKNOWLEDGMENTS

Tom Hilditch, B.Sc.Agr., is a biologist with Gartner Lee Limited. He has worked on the revegetation of pits and quarries, sandy slopes, landfills and contaminated industrial sites.

Christopher P. Hughes, F.T.Dipl., is an environmental technician with Gartner Lee Limited. His work includes the revegetation of woodwaste in northern Ontario.

CP6

Evaluating Groundwater Velocity in A Low-Permeability Fractured Shale

Kent S. Novakowski
and
John A. Cherry

Waterloo Centre for Groundwater Research
University of Waterloo
Waterloo, Ontario N2L 3G1

Introduction

Numerous landfills and industrial activities in North America are situated such that chemicals emanating from these facilities are contaminating groundwater in underlying bedrock. In particular, this is the case for sites in southern Ontario and the Niagara Peninsula where the underlying materials consist of a thin veneer of overburden overtop moderately to highly fractured shale of the Ordovician Queenston Formation or the Cambrian Georgian Bay Formation. Because contaminant migration along fracture planes within the shale can be very rapid relative to unconsolidated media, accurate prediction of the direction, velocity and dilution of the contamination is especially important with regard to public health and safety.

Groundwater velocity predictions are usually based on direct hydraulic measurements of the permeability of fractures which is expressed as an equivalent single fracture aperture, 2b. Average groundwater velocity, $\bar{v}$, is then estimated from the expression:

$$\bar{v} = \frac{\rho g (2b)^2}{12\mu} \cdot \frac{dh}{dl} \qquad (1)$$

where ρ, g and μ are the density, gravitational acceleration and dynamic viscosity of the water, respectively. The hydraulic gradient, dh/dl, is usually determined from water level measurements in piezometers or more correctly from multi-level casing strings which isolate individual fractures and fracture zones.

Equation (1) is derived from a conceptual model known as the cubic law in which water flow is between two smooth parallel plates separated by the width, 2b. Inspection of natural fractures in outcrop and core sample show that fracture surfaces are distinctly non-uniform and are characterized by a variety of aperture widths, regions where asperities contact and channels of reduced or enhanced opening. Consequently, the relationship between the 2b obtained from the results of hydraulic tests interpreted using the cubic law and the average mechanical or true aperature is unclear. This is evidenced by comparing the groundwater velocity predicted from apertures obtained from hydraulic measurement to that obtained from tracer experiments which show that hydraulically measured apertures (hereafter called hydraulic apertures) overestimate groundwater velocity in most cases (Novakowski et al., 1985; Raven et al., 1988).

The objective of this study is to investigate the relation between fracture apertures determined from hydraulic methods versus those determined using tracer experiments with the intent to resolve the role of the rough and heterogeneous character of natural fractures. This goal is addressed with a field study focussing on a single-flat lying fracture intersected by four boreholes of a seven borehole grid at a depth of about 10 m. Most common transient and steady-state single-well and multiple-well hydraulic tests were employed to determine the hydraulic aperture. The tracer apertures were determined from seven tracer experiments conducted using both injection-withdrawal and radial-convergent flow fields configurations.

Field Method

During the period of 1985 and 1986, a field site was chosen at which preliminary hydraulic tests revealed the presence of two largely unconnected flat-lying fractures at depths of 9.7 and 10.4 m below ground surface. The study site is located in Clarkson, Ontario on unused Petro-Canada property about 1.5 km north of the Lake Ontario shoreline. The fractures are in the Meaford-Dundas shale which sub-crops in the Oakville-Mississauga area of southern Ontario and strikes North-Northwest.

The initial location of the fracture set and the subsequent characterization of the apertures and boundaries were carried out over 1986 and 1987. During 1986, a preliminary drilling program was conducted in which five 76 mm boreholes were drilled 15 m apart in two perpendicular rows of three (Figure 1). Examination of the core and preliminary constant-head test results showed four main fracture zones with the shallowest set at 9.5 m to 10.5 m exhibiting the highest permeability. Subsequent field work during 1987 focused on this set and two new boreholes, UW6 and UW7 were drilled during mid-summer solely to investigate this zone. After completion of the drilling, the precise location of each of the two fractures in all seven boreholes was determined using constant-head tests with a 0.1 m interval spacing.

On the basis of the constant-head test results, the upper fracture has a mean aperture width of about 120 µm (this is equal to an hydraulic conductivity of 1×10^{-6} m/s) and the lower fracture has a mean aperture of about 200 µm (hydraulic conductivity of 5×10^{-6} m/s). Figure 1 shows the approximate extent of each fracture within the study site. The boundaries indicated on Figure 1 are arbitrary and are drawn only to show interconnection between boreholes. For example, fracture no. 1, the upper fracture, hydraulically connects UW3, UW6 and UW7 but is not well connected to UW1, UW2, UW4 and UW5. On the basis of the larger aperture identified for the lower fracture, it was selected for the purpose of this study and all further hydraulic and tracer tests described in the following text were conducted in this fracture. Preliminary estimates of hydraulic head in the lower fracture indicate groundwater flow oriented towards the northeast with a gradient of 0.01.

In addition to constant-head tests, slug tests and steady-state and transient pumping tests were also conducted. The slug tests were carried out using a straddle-packer arrangement attached to a 1.5" I.D. standpipe in which the instantaneously induced rise or fall of water level was monitored using a pressure transducer. Slug tests were conducted in all boreholes except UW6. The pumping tests were

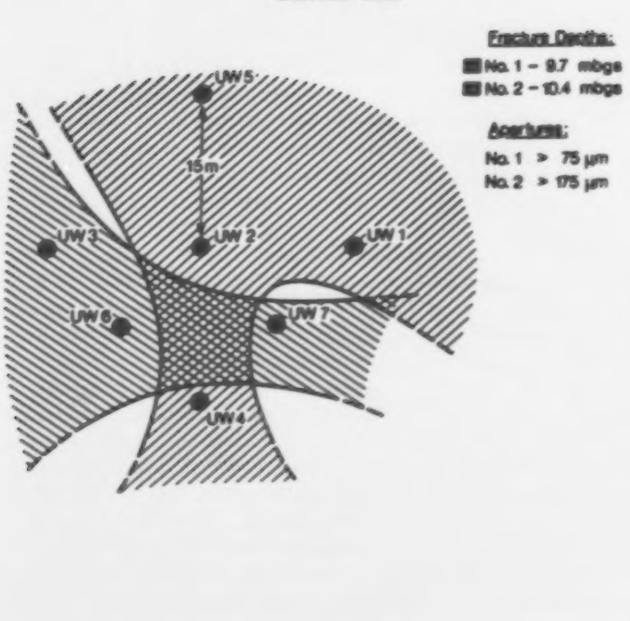
FIELD STUDY SITE
Ordovician Shale
Fracture Depths:
▨ No. 1 – 9.7 mbgs
▨ No. 2 – 10.4 mbgs
Apertures:
No. 1 > 75 µm
No. 2 > 175 µm
UW 5
15m
UW 3
UW 2
UW 1
UW 6
UW 7
UW 4

Figure 1. Approximate boundaries of the two fractures intersected by boreholes at the study site. Fracture no. 1 interconnects boreholes UW3, UW6 and UW7. Fracture no. 2 interconnects UW1, UW2, UW4, and UW5.

conducted also using a straddle packer arrangement except in this case the test fracture was completely isolated. Abstraction of water was carried out by pumping from surface through ¼" nylon tubing. Drawdown in the observation intervals also isolated by packers was monitored using pressure transducers. Pumping tests were conducted in UW5 and UW2 with observation in UW1, UW2 and UW4.

Two methods for induced-gradient tracer experiments were employed to compare to the results of the hydraulic tests; the injection-withdrawal method and the radial-convergent method. The injection-withdrawal tracer experiments were conducted by injecting water into one borehole and withdrawing water from another at the same flowrate. Sodium bromide tracer was introduced as a slug into the injection borehole once the flow field had achieved steady-state conditions. Tracer arrival at the withdrawal borehole was continuously monitored using a flow-cell arrangement and tracer concentration was measured in discrete samples of the withdrawn water. The fracture was isolated in both the injection and withdrawal boreholes using straddle packer arrangements. Injection and withdrawal flowrates and interwell hydraulic gradients were monitored on a continuing basis through the duration of each experiment. The radial-convergent tracer experiments were conducted in a similar manner except that continuous injection of water was not employed. A steady radial flow field was established around a borehole by pumping and tracer was introduced into the flow field from an observation borehole by pulse injection. Both tracer methods were employed for tests conducted between UW1 and UW2 and UW4 and UW2, with UW2 as the withdrawal borehole in all cases. The injection-withdrawal method only was employed for experiments conducted between UW2 and UW5, UW5 and UW4 and UW7 and UW3. Novakowski (1988) provides a more detailed description of the field methods employed for this study.

Results and Discussion

The constant-head hydraulic tests were analysed using the Thiem equation where the steady flow rate, Q, divided by the rise in hydraulic head, ΔH, is proportional to transmissivity, T:

$$\frac{Q}{\Delta H} = \frac{2\pi T}{\ln (r_e/r_w)} \qquad (2)$$

where r_e is the radius of influence (estimated at approximately 10 m for these tests) and r_w is the radius of the well. Fracture aperture is then calculated from the transmissivity using:

$$2b = (\frac{12\mu}{\rho g} T)^{1/3} \qquad (3)$$

Both the slug tests and transient pumping tests were analysed using type curve methods to obtain transmissivity. The steady-state pumping tests were analysed using equation (2) where the radial distance between the pumping and observation boreholes is substituted for r_e and ΔH is the difference in hydraulic head between the two wells.

The tracers experiments were analysed for fracture aperture by using analytical approximations to describe the streamline(s) between the injection and pumping borehole and solving the advection-dispersion equation along each streamline. The analytical approximations for the streamlines are based on the average travel time for the tracer and the interwell difference in hydraulic head. The aperture is determined by a trial and error procedure, varying the 2b to determine the location of the model peak.

Table 1 shows the results of the hydraulic tests and tracer experiments expressed as fracture aperture in micrometers along with the borehole interval isolated for each test. In general, distinction between the results of transient and steady-state hydraulic tests is immediately clear. The results of the transient hydraulic tests show consistently larger fracture apertures than those of the steady-state tests. This is a function of the radius of test influence and knowing that steady-state test results more likely reflect the properties of the fracture nearest the source borehole, the apertures determined from the transient tests probably reflect regions of the study fracture that have a slightly larger aperture and that are beyond the lateral extent of the study site.

On the basis of the relative uniformity of the apertures determined from the transient hydraulic tests conducted in borehole UW2 (the central borehole of the study site) there is no evidence to suggest non-radial flow effects which might indicate the presence of channeled flow. This suggests that the points of closure currently identified by boreholes UW3, UW6 and UW7 are relatively small in area and the boundaries to the fracture plane as drawn in Figure 1 are probably inappropriate.

Comparing the fracture apertures determined from the hydraulic tests to those from the tracer experiments, it is evident that the tracer apertures are consistently smaller by up to 50%. This observation is in agreement with the results of other field experiments reviewed in Raven et al. (1988). These results are significant with respect to predicting groundwater velocity in fractures because velocity is proportional to the square of the fracture aperture. Therefore, an aperture difference of a factor of 2, for example, translates into a four-fold difference in velocity.

An explanation as to why tracer apertures are always smaller than hydraulic apertures can be found based on the solute transit path length. Because we have established that natural fractures are rough and undulating, and we know that the fracture walls are in some degree of contact as evidenced by closure in UW3, UW6 and UW7, then the path travelled by the tracer in transit from the injection borehole to the pumping borehole may be very tortuous as the flow negotiates around the points of closure and areas of reduced opening.

To investigate this explanation, the tracer experiments between UW1 and UW2 and UW4 and UW2 were simulated by fixing the 2b to the size of the steady-state hydraulic aperture and modeling for the path length. Table 2 shows the modeled path lengths and values of tortuosity which are calculated by dividing the modeled path length into the actual interwell distance.

Table 1. Aperture widths (in μm) as determined from slug test, constant head test, tracer test and pumping test results.

Borehole	Aperture (μm)	Interval (mbgs)	
Slug Tests			
UW1	210	10.10 - 10.92	
UW2	267	10.16 - 10.98	
UW3	147	9.40 - 10.22	
UW4	226	10.21 - 11.03	
UW5	180	10.20 - 11.02	
UW6	-		
UW7	140	9.90 - 10.52	
Constant Head Tests			
UW1	229	9.90 - 10.72	
UW2	236	9.96 - 10.78	
UW3	135	9.10 - 9.92	
UW4	186	10.21 - 11.03	
UW5	164	9.80 - 10.62	
UW6	80	9.60 - 10.42	
UW7	120	9.30 - 10.12	
Tracer Tests			
UW1→UW2(I)	160	10.10 - 10.92	10.00 - 10.49
UW1→UW2(P)	132	10.10 - 10.92	10.00 - 10.49
UW2→UW5(I)	192	10.00 - 10.49	10.00 - 10.90
UW4→UW2(I)	155	10.20 - 11.02	10.00 - 11.49
UW4→UW2(P)	151	10.20 - 11.02	10.00 - 10.49
UW5→UW4(I)	164	10.40 - 10.89	10.20 - 11.02
UW7→UW3(I)	151	9.50 - 9.99	9.40 - 10.22
Pumping Tests			
UW5→UW2(T)	184	9.80 - 11.02	10.10 - 10.95
UW5→UW1(T)	179	9.80 - 11.02	10.10 - 10.95
UW2→UW4(S)	211	10.00 - 10.49	10.10 - 10.92
UW2→UW1(S)	215	10.00 - 10.49	10.20 - 11.02
UW2→UW1(T)	254	10.00 - 10.49	10.10 - 10.92
UW2→UW4(T)	228	10.00 - 10.49	10.10 - 10.92

T - transient
S - steady state
I - injection-withdrawal flow field
P - radial-convergent flow field

Table 2. Modeled path lengths and tortuosity determined from the tracer experiments.

	Path Length (m)	Tortuousity
UW1 to UW2(I)	19.0	0.79
UW1 to UW2(P)	23.0	0.65
UW4 to UW2(I)	20.6	0.73
UW4 to UW2(P)	20.6	0.73

The range of tortuosity is from 0.65 to 0.79 which is quite wide although not unrealistic in terms of the average angularity of flow (the vectoral direction of flow not directly towards the withdrawal well). Tortuosity of 0.65 gives an angularity of flow of 50° while 0.79 gives about 38°. The angle of flow in porous media is about 45°. Considering the complex possibility of pathways dependent on the aperture distribution, these values of tortuosity are probably reasonable.

On the basis of the results presented here and on other recent field evidence (Raven et al., 1988), it is apparent that using the cubic law to interpret the results of hydraulic tests will lead to erroneous predictions of groundwater velocity. Therefore a new conceptual model is urgently required with which the results of hydraulic tests can be utilized to predict velocity without relying on comparison to more costly and time consuming tracer experiments. On the basis of the preliminary modeling conducted for this study, it is likely that such a conceptual model will depend on the role of tortuousity during solute transport in natural fractures.

Summary

Comparisons of fracture aperture widths determined from the results of hydraulic tests and tracer experiments were made. Constant-head, slug, steady-state and transient pumping tests were employed to determine the fracture aperture, hydraulically. The tracer experiments were carried out in radial-convergent and injection-withdrawal flow field formats. The tests were conducted in a discrete flat-lying fracture in Ordovician aged shale at a depth of approximately 10 m.

The results show that apertures determined from tracer experiments are consistently smaller than those obtained from hydraulic tests. The reason for this discrepancy is probably due to the influence of tortuous flow around reduced apertures and points of closure in the fracture plane. The development of a new conceptual model which can more accurately relate the results of hydraulic tests to a prediction of groundwater velocity, is required to reconcile these differences.

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CP7

The Design and Evaluation of "*In Situ*" Biorestoration Methods for the Treatment of Sludges and Soils at Waste Disposal Sites

K.L. Berry-Spark and J.F. Barker
Institute for Groundwater Research
University of Waterloo
Waterloo, Ontario
N2L 3G1

In situ methods for treatment of waste sludges hold great promise for cost-effective, efficient remediation of sludge at waste disposal sites. An example of such a treatment scheme is the landfarming of petroleum-industry sludges, where the biodegradation and volatilization of organics and immobilization of many metals is enhanced. Whereas this treatment is successful for certain contaminants, it is ineffective for others. For sludges containing a broad spectrum of toxic organics and metals, no single remediation scheme is likely to be satisfactory.

The remediation of the diverse and complex sludges from the O.E. MacDougall Waste Disposal Site, near Brockville, Ontario, by current conventional techniques would be very costly. Natural bioremediation techniques were tested in the laboratory, using six representative soils and sludges obtained from the MacDougall site. These techniques require a minimal amount of sludge manipulation, so their use at the site is viewed as a cost-effective method of site cleanup.

Liquid industrial wastes (including solvents and waste oils), sewage sludge and septic tank wastes were disposed of in waste lagoons at the MacDougall site from 1962 to 1981. In October 1987, six samples of soil and sludge were collected for characterization of the organic chemistry of the materials. Three of the samples were brown sandy soil and three were black sludge with a strong sewage odour. No volatile organics were identified in two of the sandy soils. The remaining four samples were found to contain varying concentrations of aliphatic and aromatic hydrocarbons typical of petroleum products and chlorinated hydrocarbons typical of solvents.

In situ bioremedition is dependent upon the number and type of microorganisms present within the sludge or soil. Standard plate counts and culture tube techniques were performed to estimate the number of aerobic, anaerobic (denitrifiers, sulphate-reducers and methanogenic) and sulphate-reducing bacteria present in each material type. All sludge and soil samples contained viable bacteria of the three kinds tested for. Typically, aerobic bacteria were the most abundant, while the sulphate-reducers were the least abundant. Anaerobic bacteria were more abundant in the more contaminated sludges than in the cleaner soils.

The diverse organic chemistry and nature of the microbial population allowed the testing of a number of remedial environments in the laboratory. Bioremediation experiments employed sealed glass bottles containing soil or sludge and distilled water. Various chemical additions were made to selected bottles to establish aerobic, methane-oxidizing, denitrifying, sulphate-reducing or methanogenic conditions within the bottles. At various times, duplicate bottles were analyzed for target aromatics (benzene, toluene, xylenes, trimethylbenzene, cumene, naphthalene) and chlorinated hydrocarbon (tetrachloroethene, trichloroethene) concentrations.

Experiment 1 examined the loss of target compounds under aerobic and methane-oxidizing conditions. The concentrations of aromatics decreased over 147 days, with toluene showing the most significant concentration decrease. Tetrachloroethene and trichloroethene concentrations did not decrease with time. Oxygen concentrations decreased and carbon dioxide concentrations increased simultaneously over time. Methane concentrations showed no decrease, indicating that the methane-oxidizers were not measurably active. The aromatic losses are believed to be the result of aerobic biodegradation.

Experiment 2 was conducted to investigate the bioremediation of the sludges and soils under various anaerobic conditions. Three sludges and one soil were incubated under denitrifying, sulphate-reducing or methanogenic conditions. The most contaminated sludge showed a decrease in tetrachloroethene and trichloroethene concentrations from about 600 ug/g to less than 1 ug/g in 12 days. This decrease was accompanied by an increase in cis-1,2-dichloroethene, indicating a reductive dechlorination breakdown mechanism. Some sludges show decreases in the aromatic content. Decreases are most apparent in toluene concentrations, but trimethylbenzene and naphthalene concentrations also decreased somewhat over time. Aromatic decreases are most significant in microcosms amended with nitrate or sulphate.

In summary, the aromatic hydrocarbons are most easily broken down under aerobic conditions, but may also be degraded anaerobically upon the addition of nitrate and/or sulphate. Tetrachloroethene and trichloroethene seem to be easily broken down to dichloroethene under anaerobic conditions; however, dichloroethene seems to accumulate with time. These results are promising, since they suggest that the natural degradative processes, perhaps acting in sequence and with some stimulation, may provide significant remediation of the sludges at the MacDougall site.

CP8

Enhanced Biodegradation of Aromatic and Chlorinated Aliphatic Compounds in a Leachate-Impacted Aquifer

D.W. Acton and J.F. Barker

Waterloo Centre for Groundwater Research
University of Waterloo

A three year research study was undertaken in April 1987 to evaluate the persistence of selected organic compounds in the shallow, anaerobic leachate plume occurring in sands adjacent to a municipal landfill site in North Bay, Ontario. Research to date has focused on developing and evaluating methods for the enhanced *in situ* bioremediation of selected aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylenes, chlorobenzene, trimethylbenzene and naphthalene) and chlorinated aliphatic compounds (carbon tetrachloride, trichloroethane, and tetrachloroethylene). In previous studies of organics in landfill leachate plumes, these compounds were among the most common contaminants.

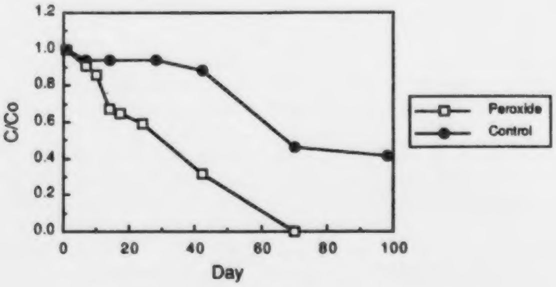
The approach of this study has been to investigate the natural persistence of the target compounds by evaluating their distribution in the landfill leachate plume, and by conducting controlled experiments simulating the actual field conditions as closely as possible. To date, laboratory microcosm experiments, *in situ* biodegradation columns, and natural gradient injection experiments have been attempted, and represent increasing degrees of realism and complexity.

Laboratory Microcosm Experiments

These experiments investigated the enhanced biodegradation of aromatic and chlorinated aliphatic compounds in aquifer material from the North Bay landfill site. Active microcosms were amended with remediating solutions of alternate electron acceptors (peroxide and nitrate) and primary substrates (glucose and acetate) to enhance natural biodegradation processes. Attenuation of organic compounds in remediated microcosms was compared to unremediated and sterile controls to assess the effectiveness of the remedial method.

Minor losses of the target compounds in sterile microcosms was attributed to sorption and diffusion. Additional mass losses in control microcosms were attributed to natural biodegradation processes. Rapid attenuation of carbon tetrachloride and accumulation of chloroform in unremediated microcosms was attributed to reductive dechlorination by anaerobic bacteria. The presence of nitrate appeared to inhibit this process. Denitrification of non-specific organic carbon was observed in nitrate-remediated microcosms, but none of the target aromatic hydrocarbons attenuated significantly. Glucose substrate addition was successful in increasing the denitrifying biomass. Significantly greater degrees of attenuation were observed in peroxide remediated microcosms, compared to unamended and nitrate-remediated microcosms (figure 1). Acetate-remediated microcosms showed no significant mass losses of the target compounds. The presence of denitrifying, sulphate-reducing, and methanogenic cultures in the microcosms was confirmed by additional tests.

Figure 1: Effect of Peroxide Addition on Toluene Biodegradation



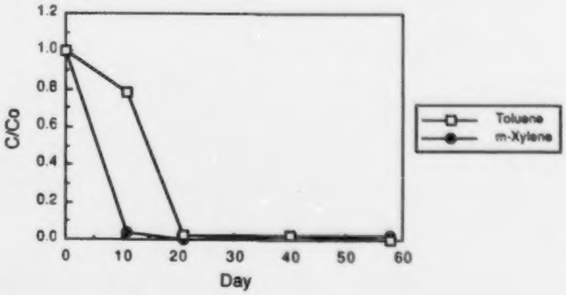
The results indicate that enhanced biodegradation of the target compounds is possible in the North Bay aquifer. Natural, unamended biodegradation of some compounds does occur in the North Bay aquifer, at much slower rates.

In situ Biodegradation Column Experiments

In situ biodegradation columns permit the investigation of enhanced biodegradation of organic compounds in a realistic field situation, while still maintaining the precise control of a laboratory experiment. The columns were pounded into the aquifer below the water table, and approximately four pore volumes of leachate was pumped out of the columns, spiked with a conservative tracer, organic compounds and remediating solutions, and then pumped back into the column. Periodic sampling of the pore water in the column allowed precise monitoring of the biodegradation processes at work in the aquifer.

Nine separate *in situ* biodegradation columns were installed at the North Bay site, which investigated both unremediated and remediated rates of biodegradation of twelve target compounds. Experiments conducted to date have investigated denitrifying, sulphate-reducing and methanogenic bacteria. The sulphate-reducing bacteria were capable of significant biotransformations of toluene and m-xylene compared to unremediated rates observed in microcosm experiments. Typical results are shown in figure 2. All of the target compounds, except carbon tetrachloride, were persistent in the nitrate-remediated columns. These results complement the findings from the laboratory microcosm experiments and represent a more realistic view of the biodegradation processes active in the North Bay aquifer.

Figure 2: Toluene and m-Xylene Biodegradation in Sulphate-Remediated Columns



Natural Gradient Injection Experiments

Natural gradient injection experiments represent the most realistic simulation of the fate of organic compounds under natural conditions. This is accomplished by introducing a large slug of water into the aquifer, spiked with a conservative tracer and organics of interest, and allowing the slug to migrate at the groundwater velocity.

Field work was undertaken at the North Bay site during the summer and fall of 1987 with the objective of performing a large scale conservative tracer injection test to establish the hydraulic aspects of the experimental site prior to conducting *in situ* biodegradation experiments. An initial sampling grid of 63 multilevel piezometers was installed at a grid spacing of 1 m and covered an area of approximately 8 m by 8 m. This network was subsequently expanded by the installation of two fences of multilevel piezometers 24 m and 36 m from the injection site.

Approximately 4800 L of city water containing 200 mg/L sodium bromide was injected over a 12 hour period in August 1987. Conductivity measurements the following day failed to indicate the presence of the plume. Samples collected from the piezometer network were analyzed for bromide, chloride and background aromatic hydrocarbon concentrations. None of the samples showed any evidence of the bromide-spiked plume.

Given the puzzling results of the large-scale injection, we concluded that the flow system in the vicinity of the injection was not as foreseen based on previous work at the site. To improve our understanding of the very local flow system, we conducted a freshwater injection experiment supplemented by an extensive aquifer coring and water table mapping program.

Coring in the area of the piezometer network revealed that the aquifer was much more heterogeneous than previously expected, with individual layers ranging from coarse sand to fine silt. Continuous monitoring during a nine hour injection of 3600 L of fresh water showed development of a 3 m by 3 m plume which migrated at approximately 1 m/day. Once developed, this plume showed evidence of vertically separating into distinct layers, due to hydraulic conductivity contrasts in the aquifer.

The extremely heterogeneous nature of the North Bay aquifer, and the fast groundwater velocities preclude the possibility of monitoring the mass balance of a large-scale injection experiment. Our efforts will now concentrate on introducing a continuous plume over an extended period, while monitoring the plume at several locations downgradient. This approach will focus on the biodegradation capabilities of the indigenous bacteria rather than the potentially complicated aspects of groundwater transport.

In summary, the research undertaken at the North Bay landfill site combines laboratory and field experiments of increasing complexity and realism to study the potential for enhanced *in situ* biodegradation of aromatic and chlorinated aliphatic compounds. The results to date demonstrate that this technique is a potentially viable alternative for remediating anaerobic, leachate-impacted aquifers.

CP9

Abstract

Waste Management Planning for Pharmaceutical Industry. R. Makhija and R.A. Stairs, Department of Chemistry, Trent University, Peterborough, ON K9J 7B8.

A study of waste management practice in the pharmaceutical industry, began by the Ministry of the Environment, has been continued by us, beginning late in 1985. A questionnaire was sent to 70 addresses. After follow-up, 35 usable replies were received, the results of which are summarized in Table I. This table includes some unsolicited information, but does not show some concerns expressed by respondents. These included categories of wastes not in the questionnaire, the need for recycling of solvents especially, and some need for education in the intricacies of the regulations. It also does not show the wastes exempted as small quantities, which may yet add up to a problem.

It became clear that the questionnaire missed much information by neglecting the use of ordinary laboratory and process chemicals and solvents. The pharmaceutical industry is part of the chemical manufacturing industry, and should have been treated as such.

Disposal practices appear to be following established guidelines. Quantities and costs are not large; the total cost is a small part of the cost of doing business. Nevertheless, concerns emerged, including the wisdom of blanket small quantity exemptions, the fate of pharmaceuticals (waste and excreted) going to sewers, and the medicines discarded by householders. A number of respondents called for economic solvent recycling facilities.

The business of waste removal shows signs of becoming a near monopoly. Two firms handled 95% of the tonnage transported.

We conclude that the wastes from this industry do not constitute a major problem in Ontario. There are, however, some questionable aspects, which should

be addressed. For that end, we make the following recommendations.

Recommendations

1. We strongly recommend that small quantity exemptions for certain pharmaceutical wastes not be allowed. This will require further work in consultation with qualified environmental toxicologists and professional personnel from the waste generators.
2. We recommend that the existing MOE Household Hazardous Waste Program should include pharmaceutical waste days in as many municipalities as possible.
3. We recommend that generators of any wastes containing substances listed in Schedules 2A and 2B be required to register under Regulation 309. This should include wastes which would otherwise be exempted as being below the small quantity limit.
4. We recommend that encouragement be given to persons or companies from the private sector to set up a cost-effective solvent recovery system.
5. We recommend that further work be undertaken in the context of the Municipal Industrial Strategy for Abatement: sewer effluents from producers of drugs deemed to be environmentally hazardous should be analyzed, and if any notable emissions are found, the effluents from sewage-disposal facilities downstream should be analyzed for the same substances, in order to determine whether they escape biodegradation.
6. We recommend that qualified persons, with assistance from the Canadian Pharmaceutical Manufacturers Association and financial support from the Ministry of the Environment, offer educational seminars to generators of pharmaceutical wastes, including manufacturers and hospitals, especially concerning Regulation 309 and the 4 R's.
7. We recommend that a correlation of the trade names, generic names and

chemical names of pharmaceutical products and ingredients should be prepared in computer-readable form, and frequently revised and updated. This would greatly facilitate cross checking of manufacturers' lists against the various Ministry schedules.

TABLE I

Major Products of Pharmaceuticals	No. of Sources	Total Quantity disposed (kg)
Antineoplastics	5	53.2
Vaccines, Biologicals	5	18,233.2
Antihistamines, Antitussives and Expectorants	9	101.15
CNS drugs, Sedatives, Analgesics, Anticonvulsants and Anaesthetics	13	2,924.9
Psychotherapeutics	7	1,390.2
Cardiovascular agents	11	758.2
Corticosteroids, Hormones, Synthetic, Estrogens	11	415.0
Antibiotics	11	1,374.15
Organic Based Pharmaceuticals Otherwise not specified	12	22,623.2
Mineral Based Pharmaceuticals Otherwise not specified	9	190,020.0
Solvents	4	1,300

INDICES LISTED FOR REFERENCE

Abstract

SESSION A: AIR QUALITY RESEARCH

Oral Presentations

A1 **Science and Policy: PhotoChemical Oxidants and Acid Bearing Species** K. L. Demerjian, Atmospheric Science Research Center, State University of New York, Albany, New York, U.S.A.

A2 **Relationship Between Forest Decline and Root Health in Ontario Sugar Maple** C. Adams, M. Egyed and T. Hutchinson*, Dept. of Botany, University of Toronto, Toronto, Ontario.

A3 **A Numerical Decline Index Rating System to Monitor Changes in Tree Condition of Hardwood Forest Species** D. McLaughlin*, W. McIlveen, W. Gizyn, D. Corrigan, R. Pearson and R. Arnup, Air Resources Branch, Environment Ontario

A4 **Investigation of Short-term Mutagenicity and Chemical Composition of Organic Solvent Extractable Fraction of Coke Oven Emission** A.J. Horton*, N. Belson, K. Shaw and G.H. Thomas, Ontario Research Foundation, Clarkson, Ontario

A5 **Quantitative Measurements of the Genetic Effects of Inhaled Carcinogens in Pulmonary Fibroblasts are Now Possible** J.A. Heddle*, A. Bouch and J.D. Gingerich, Dept. of Biology, York University, Downsview, Ontario

A6 **Sensitivity of Asthmatic Children to Air Pollution;** D. Pengelly* and C. Goldsmith, McMaster University, Hamilton, Ontario

A7 **Hazardous Contaminants in Ontario: Environmental Fate and Human Exposure** D. Mackay* and S. Paterson, Institute for Environmental Studies, University of Toronto, Toronto, Ontario

Abstract

SESSION A: AIR QUALITY RESEARCH

Oral Presentations

A8 **Verification of the Cloud and Wet Deposition Fields of a MesoScale Model of Long-Range Transport of Air Pollutants** H.R. Cho*, S.T. Soong and J.V. Iribarne, Department of Physics, University of Toronto, Toronto, Ontario

A9 **Eulerian Model Evaluation** M. Alvo, Department of Mathematics, University of Ottawa, Ottawa, Ontario

A10 **Scale Model Studies and Development of Prediction Procedures for Heavy Gas Dispersion in Complex Terrain 1988** P. A. Irwin*, M.C. Murphy and K. C. Heidorn, Rowan Williams Davies and Irwin Inc., Guelph, Ontario

A11 **An Investigation of Wind Generated Particle Transport Rates within a Turbulent Boundary-Layer** A.D. Ciccone*, J.G. Kawall and J.F. Keffer, Department of Mechanical Engineering, University of Toronto, Toronto, Ontario

A12 **Incineration of Wastes** K. Davies, Environmental Protection Office, City of Toronto, Toronto, Ontario

A13 **Detectability of Step Trends in the Rate of Atmospheric Sulphate Deposition** E.A. McBean*, M.G. Kompter and G.J. Farquhar, Department of Civil Engineering, University of Waterloo, Waterloo, Ontario

A14 **Incinerator and Steel Plant Contributions to Air Particulates as Determined by Size-Specific Receptor Modelling** A.C. Chan*, Z-J. Kang and R.E. Jervis, Dept. of Chemical Engineering, University of Toronto, Toronto, Ontario

Abstract

SESSION A: AIR QUALITY RESEARCH

Oral Presentations

A15 **A Study on the Sources of Acid Precipitation in Ontario, Canada** P.K. Hopke* and Y. Zeng, Department of Civil Engineering, University of Illinois, Urbana, Illinois, U.S.A.

A16 **Advanced Techniques for Mobile Monitoring of Trace Organics in Air** G.B. De Brou*, E. Singer, M.A. Sage, R.W. Bell, R.E. Chapman and D.J. Ogner, Air Resources Branch, Environment Ontario

A17 **Atmospheric Trace Gas Measurements Using a Tunable Diode Laser Absorption Spectrometer** D.R. Hastie* and H.I. Schiff, Department of Chemistry, York University, Downsview, Ontario

A18 **Biomedical Waste Incineration Testing Program** V. Ozvacic*, G. Wong, G. Marson, R. Clement, D. Rokosh, S. Suter, G. Horsnell, J.C. Hipfner, S. Burns and H. Corinthios, Environment Ontario

A19 **A Study of High Temperature Photochemical Kinetics of Sulphur Dioxide and Nitrogen Oxides For a Flue Gas Treatment Process** J. Hunt*, P. Fellin, K.A. Brice, D. Ernst, D. Glendenning and R. Caton, Concord Scientific, Toronto, and C. Fung and K. Smith, Environment Ontario

A20 **Modelling the Photochemical Decomposition of Chlorinated Phenols by Sunlight** N.J. Bunce* and J.S. Nakai, Dept. of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario

Abstract

SESSION A: AIR QUALITY RESEARCH

Poster Presentations

AP1 Stochastic Modelling of Dispersion from Single Elevated Sources E. Robertson and P. J. Barry, Atomic Energy of Canada Limited, Chalk River Nuclear Laboratories, Chalk River, Ontario

AP2 Feasibility Study for Assessing and Modelling Microclimatic Conditions on the Fonthill Kame (Phase 1) T. B. Shaw, Brock University, St. Catharines, Ontario

AP3 Critical Evaluation of Atmospheric Pollutant Parameterization from Satellite Imagery N. T. O'Neill, A. Royer and L. Hubert, Universite de Sherbrooke, Sherbrooke, Quebec, and J. Miller and J. Freemantle, CRESS, York University, Downsview', ', Ontario, and G. Austin and A. Davis, McGill

AP4 A 3-D Mesoscale Wind Field Model and its Application for Emergency Planning at Nuclear Power Plants in Ontario
H. Sahota, P. K. Misra, R. Bloxam and D. Rhee, Air Resources Branch, Environment Ontario

AP5 The Results from a Meso-scale Model M. Niewiadomski, University of Toronto, Toronto, Ontario

AP6 Dose Response for Selected Environmental Air Pollutants: Results from a Study on Runners R. B. Urch, F. Silverman, P. Corey and R. J. Shephard, The Gage Research Institute, University of Toronto, Toronto, Ontario

Abstract

SESSION A: AIR QUALITY RESEARCH

Poster Presentations

AP7 **Hamilton Air: Chemical Composition and Genotoxic Activity of Respirable Particulate and Organic Vapours** D.W. Bryant, C. Kaiser-Farrell and D.R. McCalla, Department of Biochemistry, McMaster University, Hamilton, Ontario

AP8 **Mutagenicity Studies and Risk Estimation of Complex Mixtures of Organic Airborne Contaminants** A.S. Raj and D.M. Logan, Department of Biology, York University, Downsview, Ontario

AP9 **In-Situ Monitoring of the Environment for Genotoxicity Levels Using Rodents** M. Petras, M. Vrzoc, S. Meddins, K. Hill and T. Sands, Department of Biological Sciences, University of Windsor, Windsor, Ontario

AP10 **Method Development for the Monitoring and Analysis of Odorous Organics in Ambient Air** C.C. Chan, L. Vainer and J.W. Martin, Mann Testing Laboratories Ltd., Mississauga, Ontario, and A. Szakolcai and B. Foster, Environment Ontario

AP11 **Gas Phase Analysis of Organic Compounds from Structural Domain Modulation within Flourescent Lipid Multilayers** U.J. Krull, R.S. Brown and K. Stewart, Department of Chemistry, Erindale Campus, University of Toronto, Mississauga, Ontario

AP12 **Atmospheric Measurements of Natural Hydrocarbons Using Gas Chromatography/Mass Spectrometry** H. Niki and B.H. Khouw, Department of Chemistry and Centre for Atmospheric Chemistry, York University, Downsview, Ontario

Abstract

SESSION A: AIR QUALITY RESEARCH

Poster Presentations

AP13 Utilization of Established Air Pollution Monitoring Networks in Ontario Following Nuclear Incidents J.A. Slade and G. Laszlo, Radiation and Industrial Safety Branch, Atomic Energy of Canada Limited, Chalk River, Ontario

AP14 A Re-Examination of Ontario's 24 Hour Ambient Air Quality Criterion for Hydrogen Fluoride R.D. Jones and D.S. Harper, Air Resources Branch, Environment Ontario

AP15 Production of Ozone-insensitive White Bean Varieties T.E. Michaels, Department of Crop Science, University of Guelph, Guelph, Ontario

AP16 Efficacy of Film-forming Chemicals for Protecting Roadside Trees Against Salt Spray C. Chong, Ministry of Agriculture and Food, Horticultural Research Institute of Ontario, Vineland Station, Ontario

AP17 An Evaluation of the Problems of Particulate Emission from the Wood Products Industry M.F. Lepage and A.E. Davies, Rowan Williams Davies & Irwin Inc., Guelph, Ontario

AP18 Relationship of Sugar Maple Decline and Corresponding Chemical Changes in Xylem Sap Carbohydrates, Micronutrients and Trace Elements S.N. Pathak, T. Hutchinson and D.N. Roy, Department of Forestry, University of Toronto, Toronto, Ontario

AP19 Identification of Long Range Aerosol Sources at the Dorset Environment Station J. Drake, A. Kabir and S. Vermette, Department of Geography, McMaster University, Hamilton, Ontario

Abstract

SESSION B: WATER QUALITY RESEARCH

Oral Presentations

B1 **Aquatic Biology in the New Regulatory Framework** K. Day, National Water Reseach Institute, Burlington, Ontario.

B2 **Hypothesis Testing in Aquatic Toxicology: QSAR Relationships and Simple Kinetic Modelling** L. S. McCarty*, University of Waterloo, Waterloo, Ontario, G. W. Ozburn and A. D. Smith, Lakehead University, Thunder Bay, Ontario.

B3 **Variations in the Response of Fish Population Characteristics to Environmental Changes** K. R. Munkittrick* and D. G. Dixon, Department of Biology, Universityof Waterloo, Waterloo, Ontario.

B4 **An Examination of Chronic Toxicity of Thiocyanate to Freshwater Fish for the Development of a Water Quality Criterion** D. G. Dixon, R. P. Lanno* and S. D. Kevan, University of Waterloo, Waterloo, Ontario.

B5 **Potential Role of Polycyclic Aromatic Hydrocarbons in the Development of Liver Tumors in Fish from Polluted Sites of Lake Ontario** G. M. Kirby, I. R. Smith, C. Thorn, H. W. Ferguson and M. A. Hayes*, Univeristy of Guelph, Guelph Ontario.

B6 **Plant Bioassays for the Detection of Environmental Mutagens in an Aquatic Environment** W. F. Grant, Department of Biology, York University, Downsview, Ontario.

B7 **Effects of Temperature and Field Procedures on PCB Bioaccumulation in Elliptio Complanata** A. Melkic* and Y. Rollin, Intergrated Explorations, Guelph, Ontario.

Abstract

SESSION B: WATER QUALITY RESEARCH

Oral Presentations

B8 Biomonitoring: Chemical Dependent Quantitative Relationships for the Body Burdens of Organic Chemicals in Aquatic Biomonitors F. Gobas*, R. Russell and G. Haffner, Great Lakes Institute, Univerisity of Windsor, Windsor, Ontario.

B9 Biomonitoring Protocols for Adult Aquatic Insects: Seasonal Availability, Sample Size and Sensitivity Z. E. Kovats and J. J. H. Ciborowski*, Dept. of Biological Sciences, University of Windsor, Windsor, Ontario.

B10 An Ecosystem Approach to the Monitoring of PCB's in Pristine Ontario Lakes C. D. Metcalfe* and C. R. Macdonald, Trent University, Peterborough, Ontario.

B11 Metal Contamination of Wetland Foodchains in the Bay of Quinte, Ontario A. Crowder*, W. Dushenko and J. Greig, Dept. of Biology, Queen's University, Kingston, Ontario.

B12 An Overview of Aquatic Environmental Research in Quebec M. Slivitsky, INRS-EAU, Ste. Foy, Quebec.

B13 Development of an Improved System for the Application of Powdered Activated Carbon in Water Treatment Plants H. Donison*, A. Benedek and J. J. Bancsi, Zenon Environmental Inc., Burlington, Ontario.

B14 Municipal Utilization of Water Demand Management Strategies in Ontario Municipalities R. D. Kreutzwiser* and R. B. Feagan, Dept. of Geography, University of Guelph, Ontario.

Abstract

SESSION B: WATER QUALITY RESEARCH

Oral Presentations

B15 **A Preliminary Study to Determine the Feasibility of Medium Pressure Mercury Lamps for Disinfecting Low Quality Wastewaters** G.E. Whitby and G. Sakamoto, Trojan Technologies Inc., London, Ontario, and G. Palamateer*, Envioronment Ontario.

B16 **Characterization of the Fecal Indicator Bacterial Flora of Sanitary Sewage with Application to Identifying the Presence of Sanitary Waste in Storm Sewers** P.L. Seyfried*, T. Bleier, Y. Xu and R. Harmandayan, University of Toronto, Toronto, Ontario.

B17 **Landsat-5 TM Spectral Responses for Lakes Across Northeastern Ontario** J.R. Pitblado, Geography Department, Laurentian University, Sudbury, Ontario.

B18 **Relationship of Mercury Levels in Sportfish with Lake Sediment and Water Quality Variables** C.D. Wren, B.A.R. Environmental, Quelph, Ontario.

B19 **Trend Analysis Procedures for Water Quality Time Series** A.I. McLeod*, and K.W. Hipel, McLeod-Hipel Associates Ltd., London, Ontario and B. Bodo, Environment Ontario.

B20 **Use of a Bromobenzoate for Cross-Adaptation of Anaerobic Bacteria in Lake Ontario Sediments for Biodegradation of Chlorinated Aromatics** M. Urbanek*, T. Strycek, R.C. Wyndham and M. Goldner, University of Toronto, Toronto, Ontario.

Abstract

SESSION B: WATER QUALITY RESEARCH

Poster Presentations

BP1 **The Effects of Agricultural Drainage on Sediment and Water Quality Loadings** W.E. Watt, Department of Civil Engineering, Queen's University, Kingston, Ontario.

BP2 **WATQUAS 2.0: An Expert System for the Water Quality Assessment of Ontario Rivers** W.C. Allison and T.E. Unny, Department of Civil Engineering, University of Waterloo, Waterloo, Ontario, and L. Logan, Environment Ontario.

BP3 **Geochemical Characterization, Size Fractionation and Bioavailability of Trace Metal Particulate Associations in the Don River** L. Warren and A.P. Zimmerman, Department of Zoology, University of Toronto, Toronto, Ontario.

BP4 **The Investigation, Evaluation and Recommendation of Biomonitoring Organisms for Procedures Development for Environmental Monitoring** C.A. Jefferson, Curry-Jefferson Environmental Services, Port Perry, Ontario.

BP5 **The Ontario Inland Lakes Program and Management of Blue-Green Algae: Three Whole Lake Treatments in 1988** H. Vandermeulen and K.H. Nicholls, Water Resources Branch, Environment Ontario.

BP6 **Characterization of the Grazing Fauna Within Five Softwater Lakes With Respect to Accumulations of Metaphytic Filamentous Algae** P.M Stokes, E.T. Howell and R.L. France, Institute for Environmental Studies, University of Toronto, Toronto, Ontario.

Abstract

SESSION B: WATER QUALITY RESEARCH

Poster Presentations

BP7 **Sedimentary Chrysophycean Cyst Assemblages as Paleoindicators in Acid Sensitive Lakes** M. Rybak and I. Rybak, ARECO Canada Inc., Ottawa, Ontario, and K. Nicholls, Environment Ontario.

BP8 **Factors Regulating Contaminant Levels In Forage Fish Species** C.E. Herbert and G.D. Haffner, Great Lakes Institute, University ofWindsor, Windsor, Ontario.

BP9 **The Isotopic Composition of Upland Forest Soil Sulphate** D.R. Van Stempvoort and P. Fritz, Department of Earth Science, University of Waterloo, Waterloo, Ontario.

BP10 **Recent Trends and Historical Changes in Water Quality of Lake Muskoka** M. Rybak and I. Rybak, ARECO Canada Inc., Ottawa, Ontario, and K. Nicholls, Environment Ontario.

BP11 **In-Situ Determination of Fecal Indicator Bacterial Survival in Agriculturally-Impacted Watersheds** M.J. Walters, Lake Simcoe Region Conservation Authority, Newmarket, Ontario.

BP12 **Development of an Acute and Chronic Sediment Bioassay Protocol Using Larval Mayflies and Juvenile Fathead Minnows** G. Krantzberg and R. Pope, University of Toronto, Toronto, Ontario.

BP13 **Three Hour Pulse Exposure of Potassium Thiocyanate to Rainbow Trout Eggs Before and After Water Hardening** S. Kevan And G. Dixon, University of Waterloo, Waterloo, Ontario.

Abstract

SESSION D: ANALYTICAL METHODS

Oral Presentations

D1 **Analytical Chemistry in a Regulatory Environment** R. Kagel, Dow Chemicals, Midland, Michigan, U.S.A.

D2 **Adaptation of Water Preconcentration Techniques Developed for PCDD Analysis to Other Target Organic Pollutants.** E. Dowdall*, B.R. Hollebone, L. Brownlee and C. Shewchuk, Carleton University, Ottawa, Ontario.

D3 **The Purpose and Significance of Ultratrace Analysis of Dibenzo-p-Dioxins: The Concept of Risk** L. Brownlee* and B.R. Hollebone, Chemistry Department, Carleton University, Ottawa, Ontario.

D4 **Procedures for the Analysis of 2,3,7,8-Substituted PCDD & PCDF Isomers and Other Target Compounds in Environmental Samples** F.W. Karasek*, T.S. Thompson and K.P. Naikwadi, University of Waterloo, Waterloo, Ontario.

D5 **The Closed-Loop Stripping Technique, Applied to Potable Water to Solve Taste and Odour Problems** J.P. Palmentier*, D. Robinson and V. Taguchi, Laboratory Services Branch, Environment Ontario.

D6 **Solid Supported Processes in Environmental Analysis** J.M. Rosenfeld, Department of Pathology, McMaster University, Hamilton, Ontario.

D7 **Synthesis and Use of Liquid Crystalline Polysiloxane Substrate in Capillary Column GC-MS for Isomer Specific Separation of Toxic Isomers of PCDD and PCDF** K.P. Naikwadi* and F.W. Karasek, University of Waterloo, Waterloo, Ontario.

Abstract

SESSION D: ANALAYTICAL METHODS

Oral Presentations

D8 **Development of Mobile Infrared Spectroscopy for On-site Speciation of Organic Wastes** P. Yang* and J. Osborne, Laboratory Services Branch, Environment Ontario.

D9 **Mobile Laboratory: On the Development and Real World Application Aspects** D. Toner*, B. Dalton, D. Morse, K. Hom, P. Yang and J. Osborne, Laboratory Services Branch, Environment Ontario.

D10 **Regiospecific Synthesis of All Isomeric Nitrofluorenones and Nitrofluorenes by Transition Metal Catalyzed Cross Coupling Reactions** V. Snieckus*, T. Iihama, J.-m Fu and M. Bourguignon, University of Waterloo, Waterloo, Ontario.

D11 **Preparation of Heterocyclic Polynuclear Aromatic Compounds as Analytical Standards** E. Lee-Ruff*, B.E. George, F.J. Ablenas and Y.S. Chung, Department of Chemistry, York University, Downsview, Ontario.

D12 **Application of ICP Spectrometry in Health and Environment: A Case Study of Soil Ingested by Children** R. Barnes, University of Massachusetts, Amherst, Massachusetts, U.S.A.

D13 **Direct Sample Insertion into an Inductively Coupled Plasma for Atomic Emission and Mass Spectrometry** L. Blain* and E.D. Salin, Department of Chemistry, McGill University, Montreal, Quebec.

Abstract

SESSION D: ANALYTICAL METHODS

Oral Presentations

D14 Analysis of Germanium and Tin by Hydride Generation D.C. Plasma Atomic Emission Spectrometry: Application to Determinations of Germanium and Tin in Air Filters I.D. Brindle*, B. Buchanan and X-c. Le, Brock University, St. Catharines, Ontario.

D15 Use of the Hot Slurry Technique for Solid Sample Introduction for ICP-AES L. Gervais* and E.D. Salin, Department of Chemistry, McGill University, Montreal, Quebec.

D16 Advanced Technology for Destruction of Waterborne Organic Pollutants H. Al-Ekabi* and M. Robertson, Nulite, A Division of Nutech Energy System Inc., London, Ontario.

D17 Development of ACexpert 2: Implementation of an Expert System for Automated Metal Analysis by Atomic Absorption Spectroscopy M.J. Stillman*, T.A. Cox and W.R. Browett, University of Western Ontario, London, Ontario.

D18 Adaptation of Water Preconcentration Techniques of Trace Metal Detection K.L. Singfield*, B.R. Hollebone, L.J. Brownlee, Dept. of Chemistry, Carleton University, Ottawa, Ontario, and P. Vijan, Environment Ontario.

D19 Comparison of Various Leachate Extraction Procedures for the Characterization of Inorganics in Wastes J.R. Kramer*, P. Brassard, J. Gleed and P.V. Collins, Department of Geology, McMaster University, Hamilton, Ontario.

Abstract

SESSION D: ANALYTICAL METHODS

Oral Presentations

D20 **2,4-Dichlorophenoxylacetic Acid (2,4-D) Determination in Water, Urine and Soil Extracts by Enzyme Immunoassay (EIA) and Radioimmunoassay (RIA)**
J.C. Hall* and K. Krieg, Dept. of Environmental Biology, Universityof Guelph, Guelph, Ontario.

Abstract

SESSION D: ANALAYTICAL METHODS

Poster Presentations

DP1 **Derivatization of Acidic Organic Compounds Using Phase Transfer Catalysis** V.Y. Taguchi and O.W. Berg, Laboratory Services Branch, EnvironmentOntario.

DP2 **New Chemical Ionization Reagents Directed Toward Mass Spectrometric Analysis of Trace Organics** T.B. McMahon, K. Froese and C.E. Allison, Department of Chemistry and Guelph-Waterloo Centre for Graduate Work in Chemistry, University of ', 'Waterloo, Waterloo, Ontario.

DP3 **An Interrupted Segemented Flow Stream Microwave', 'Solid Sample Decomposition for ICP-AES** E.D. Salin And B. Liu, Department of Chemistry, McGill University, Montreal, Quebec.

DP4 **Solid Phase Extraction of PAH's From Drinking Water and Analysis of Chlorophenols and Phenoxy-acid Herbicides in Water** W.G. Craig and C.D. Hall, Paracel Laboratories Ltd., Nepean, Ontario.

DP5 **Automated Water Preconcentration Sampler for Dioxin Detection at the Parts Per Quadrillion Level** C. Shewchuk, B. Hollebone, L. Brownlee and E. Dowdall, Carleton University, Ottawa, Ontario, and R. Hunsinger, M. Uza, H. Tosine and S. Suter, Environment Ontario.

DP6 **Automated HPLC Method for Low Level Polynuclear', 'Aromatic Hydrocarbon (PAH) Analysis of Drinking Water** P.W. Crozier and C.D. Hall, Laboratory Services Branch, EnvironmentOntario.

Abstract

SESSION D: ANALYTICAL METHODS

Poster Presentations

DP7 **Supercritical Fluid Extraction of Trace Organics From Solid Matrices** P. Kruus and R. C. Burk, Department of Chemistry, Carleton University, Ottawa, Ontario and G. Crawford, Laboratory Services Branch, Environment Ontario.

DP8 **Automated Sample Introduction and Pretreatment', 'with Flow Injection ICP-ES** J.F. Hopper, F. Mo and D.W. Boomer, Laboratory Services Branch, Environment Ontario.

DP9 **Applications of Flow Injection Technology to ICP-MS** M.J. Powell, J.F. Hopper and D.W. Boomer, Laboratory Services Branch, Environment Ontario.

DP10 **Investigation of the In-Situ Acetylation Process and its Applicability to the Analysis of a Wide Range of Phenolic Compounds in Water** R. Lega, O. Meresz and M. Savu, Laboratory Services Branch, Environment Ontario.

DP11 **Robustness of the Student's T-test with Censored Environmental Quality Data** E.E. Creese, Creese Environmental Consulting, Waterloo, Ontario.

DP12 **Automation of Solid Supported Reactions by Robotics** J.M. Rosenfeld and E. Pevolinas, McMaster University, Hamilton, Ontario.

Abstract

SESSION E: ENVIRONMENTAL ECONOMICS

Oral Presentations

E1 **Understanding Environmental-Economic Integration** P.A. Victor, VHB Research Ltd., Toronto, Ontario.

E2 **Economic Valuation Disparities and Environmental Policies** J.L. Knetsch, Economics Department, Simon Fraser University, Burnaby, British Columbia.

E3 **The Physco-social Impacts of Exposure to Environmental Contaminants in Ontario: A Feasibility Study** S.M. Taylor*, J. Frank, M. Haight, D. Streiner, S. Walter and N. White, McMaster University, Hamilton, Ontario.

E4 **Economic Assessments of MISA Regulations for Direct Industrial Dischargers in Ontario** O.E. Salamon* and J.A. Donnan, Policy and Planning Branch, Environment Ontario.

E5 **The Extra Strength Sewer Surcharge to Regulate Industrial Sanitary Waste Discharges** M. Fortin*, Ecologistics, Waterloo, Ontario, G. Zudovs, CANVIRO, and J. Donnan and G. Zegarac, Environment Ontario.

E6 **A Study of the Economic Factors Relating to the Implementation of Resource Recycling or Zero-Discharge Technologies for Heavy Metal Generating Industries in Canada** B. Fleet*, J. Kassirer, T. Burrell, T. Sanger, C. Small and B. Cardoza, University of Toronto, Toronto, Ontario.

E7 **Determinants of Participation in Solid Waste Source-Separation Programs in High-Rise Apartment Buildings** V.W. Maclaren, Department of Geography, University of Toronto, Toronto, Ontario.

Abstract

SESSION E: ENVIRONMENTAL ECONOMICS

Poster Presentations

EP1 **The New Economics of Sustainable Development** R. Z. Rivers, Water Planning and Management Branch, Canada Centre For Inland Waters, Environment Canada, Burlington, Ontario.

EP2 **The Environmental Effects of Forestry Operations in Ontario: How Much Do We Know?** J. A. Dunster, Federation of Ontario Naturalists, Toronto, Ontario.